FUNDAMENTALS
OF
CHEMICAL
PROBLEMS

Dr. B. K. MUKHERJEE

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FUNDAMENTALS OF CHEMICAL PROBLEMS

For

[I. I. T. Admission Test.; J. E.; I. S. C.; All India H. S.;
H. S. C. (General and Vocational); I. Sc. and 2yr B. Sc.
(Pass) Examination.)

By

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PREFACE

As a result of my experience of over 17 years as a teacher in one of the renowned colleges of the State of West Bengal, I have come to realize that the students in H. S. ; I. S. S. C and I. Sc. stages in particular and even in B. Sc. level feel shy of solving numerical problems in Chemistry. They, therefore, lack a proper understanding of the subject and also are unable to get good marks in the Examination.

The book entitled "Fundamentals of Chemical Problems" deals with the problems on almost all topics in Chemistry. Before attempting the solution to the problems, the theoretical aspect is covered briefly in each chapter. This book would also be useful to the students who intend to appear for various competitive public Examinations (I. I. T ; J. E ; Civil service etc). A large number of problems, set in the latest different University papers particularly from the year 1970 to 1980, have been included to get an idea of the type of problems asked in such Examinations. The problems for practice given at the end of each chapter will enable the students to test his understanding and help to acquire skill in getting the solutions of many typical problems.

Due to shortage of time in publication, some errors might have crept in for which I seek apology from the readers. I have put in my best effort to make the book increasingly valuable for the students. While I hope that this publication will be appreciated by the readers, any concrete suggestions for further improvement of the book will be cordially welcome. I have not adequate words to express thanks to the B. Chand & Sons, Calcutta, publishers and their printers for the excellent set up in which the book has been fabricated. The preface will remain incomplete if I fail to show my gratitude my father Prof. Bibhuti Bhushan Mukherjee, Retired Professor of Chemistry and Industrial Chemist, Kokar (Jatratar), Ranchi, Behar for whose constant encouragement for writing the book has come finally on the prints. Last but not the least I express thanks to my wife Smt. Puspita Mukherjee and my son Sri Bidyut Mukherjee for giving constant encouragement for writing this book,

Calcutta
Daljatra
20th March, 1981.

B. K. Mukherjee

Dedicated to my grand father Late Prof. (Dr.) Mahomapadhya Vagbat Kumar Sastri, first Ashutosh Chair Holder of Calcutta University.

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Atomic Weight Table

At. No. & Symbol	Element	At. Wt.
1 H	Hydrogen	1·0080
2 He	Helium	4·0030
3 Li	Lithium	6·940
4 Be	Beryllium	9.013
5 B	Boron	10·82
6 C	Carbon	12·011
7 N	Nitrogen	14·008
8 O	Oxygen	16·0000
9 F	Fluorine	19·00
10 Ne	Neon	20·183
11 Na	Sodium	22·991
12 Mg	Magnesium	24·32
13 Al	Aluminium	26·98
14 Si	Silicon	28·09
15 P	Phosphorus	30·975
16 S	Sulphur	32·066
17 Cl	Chlorine	35·457
18 A	Argon	39·944
19 K	Potassium	39·100
20 Ca	Calcium	40·08
21 Sc	Scandium	44·96
22 Ti	Titanium	47·90
23 F	Vanadium	50·95
24 Cr	Chromium	52·01
25 Mn	Manganese	54·94
26 Fe	Iron	55·85
27 Co	Cobalt	58·94
28 Ni	Nickel	58·71
29 Cu	Copper	63·54
30 Zn	Zinc	65·38
31 Ga	Gallium	69·72
32 Ge	Germanium	72·60
33 As	Arsenic	74·91
34 Se	Selenium	78·96
35 Br	Bromine	79·916
36 Kr	Krypton	83·80
37 Rb	Rubidium	85·48
38 Sr	Strontium	87·63
39 Y	Yttrium	88·92
40 Zr	Zirconium	91·22
41 Nb	Niobium	92·91
42 Mo	Molybdenum	95·95
43 Tc	Technetium	(99)
44 Ru	Ruthenium	101·1
45 Rh	Rhodium	102·91
46 Pd	Palladium	105·4
47 Ag	Silver	107·880
48 Cd	Cadmium	112·41
49 Indium	Indium	114·82
50 Sn	Tin	118·70
51 Sb	Antimony	121·76

FUNDAMENTALS OF CHEMICAL PROBLEMS

CHAPTER I

Problems on Gas Laws, Dalton's law of partial pressures, Avogadro's hypothesis, Molecular weight and mole concept.

Theory :

(A) **Boyle's law :** Temperature remaining constant, the volume of a given mass of a gas varies inversely as the pressure. The law can be stated mathematically as,

$V \propto \frac{1}{P}$ or $V = \text{constant}\frac{1}{P}$. Where, P = pressure exerted by gas molecules.

V = Volume of the vessel

= Volume for movement of gas molecules.

T = Absolute temperature of the gas.

$\therefore$ $PV = \text{constant}$. When T is kept constant.

From Boyle's law, $P_1V_1 = P_2V_2$.

Where, P_1 = Initial pressure ; P_2 = Final pressure.

V_1 = Initial volume ; V_2 = Final volume.

Density $\propto \frac{1}{\text{Volume}}$, when mass is fixed. $\because$ Density $= \frac{\text{Mass}}{\text{Volume}}$.

$\therefore$ Pressure $\propto$ Density

$\frac{P_1}{D_1} = \frac{P_2}{D_2}$. Where, D_1 = Initial density ;

D_2 = Final density.

or $\frac{D_1}{D_2} = \frac{P_1}{P_2}$.

(B) **Charles' Law :** Pressure remaining constant, the volume of a given mass of a gas increases or decreases by $\frac{1}{273}$ of its volume at 0°C for 1°C rise or fall in temperature. Mathematically the law can be expressed in following equation.

$$V_{t_1} = V_0 + \frac{1}{273}V_0t_1 = V_0\left(1 + \frac{t_1}{273}\right) = V_0\left(\frac{273 + t_1}{273}\right).$$

Where, V_0 = Volume of gas at 0°C ; Vt_1 = volume at t_1°C.

Similarly; $Vt_2 = V_0\left(\frac{273+t_2}{273}\right)$; Vt_2 = volume at t_2°C.

$$\therefore \frac{Vt_1}{Vt_2} = \frac{273+t_1}{273+t_2}$$

or $\frac{Vt_1}{Vt_2} = \frac{T_1}{T_2}$. Where, $T_1 = 273+t_1$ = temperature in absolute degree. $T_2 = 273+t_2$ = Do.

Alternatively, the law can be stated as, pressure remaining constant, the volume of a given mass of a gas varies directly with the absolute temperature (°A or °K according to Kelvin).

Thus, $\frac{V_1}{V_2} = \frac{T_1}{T_2}$. Where, $V_1 = Vt_1$; $V_2 = Vt_2$; P is kept constant.

or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

$\because D \propto \frac{1}{V}$. Where, D = Density of the gas.

$V \propto T$.

$$\therefore \frac{D_2}{T_1} = \frac{D_1}{T_2}.$$

$$\text{or} \quad \frac{D_2}{D_1} = \frac{T_1}{T_2}.$$

(C) Gas equation : By combining Boyle's law and Charles' law, we can write

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}.$$

$$\because D \propto \frac{1}{V}.$$

$$\therefore \frac{P_1D_2}{T_1} = \frac{P_2D_1}{T_2}.$$

$PV = RT$ is known as ideal gas equation for **1** gm. mole of an ideal gas. 1 gm. mole is the molecular weight, expressed in grammes. R is called molar gas constant or the gas constant. $PV = n\,RT$ for n gm. moles of an ideal gas.

$PV = \frac{W}{M} RT$ for n gm. moles of an ideal gas.

Where, W = Weight in gms. of an ideal gas ; M = Molecular weight of the ideal gas. $P=\frac{W}{V}\cdot\frac{1}{M}RT=\frac{D}{M}RT.$ $\because$ $D=\frac{W}{V}.$

(D) Numerical values of R :

(With the help of Avogadro's hypothesis)

The numerical value of R is calculated from the equation $R=\frac{PV}{T}$, employing the fact that at 0°C and at a pressure of 1 atm. (N. T. P. or S. T. P.), the volume occupied by 1 gm. mole of an ideal gas is 22·4 litres, (Vide. Avogadro's hypothesis). The value of R varies with the units in which P, V and T are expressed. Thus, if P, V and T are expressed in atms., litres and absolute degree respectively, the value of R can be calculated as follows :

$P=1$ atm ; $V=22{\cdot}4$ litres ; $T=273°A$.

$$R=\frac{PV}{T}=\frac{1\times 22{\cdot}4}{273}=0{\cdot}0821 \text{ litre.atm.deg}^{-1}\text{.mole}^{-1}.$$

If P is expressed in dynes per square centimeter and V in cc., we have, $P=76\times 13{\cdot}6\times 981$ dynes/sq. cms.

$V=22{\cdot}4\times 1000=22400$ cc., $T=273°A$.

$$R=\frac{PV}{T}=\frac{76\times 13{\cdot}6\times 981\times 22400}{273}=8.32\times 10^{7} \text{ ergs.deg}^{-1}\text{.mole}^{-1}.$$

Since, 1 calorie $=4{\cdot}18\times 10^{7}$ ergs ;

$$R=\frac{8{\cdot}32\times 10^{7}}{4{\cdot}18\times 10^{7}}=1{\cdot}99\simeq 2 \text{ cals.deg}^{-1}\text{.mole}^{-1}.$$

Also, 1 Joule $=10^{7}$ ergs, $R=8{\cdot}0$ Joule.deg^{-1}.mole^{-1}.

(E) Dalton's law of partial pressures :

From Dalton's law of partial pressures,

$P=p_1+p_2+p_3+\cdots\cdots$

$PV=nRT$; $p_1V=n_1RT$; $p_2V=n_2RT$; $p_3V=n_3RT$.

P = Total pressure, exerted by an ideal gas mixture.

V = Volume of the vessel containing the ideal gas mixture.

T = Temperature of the ideal gas mixture.

p_1, p_2, p_3 etc are partial pressures, contributed by the components of the ideal gas mixture. n_1, n_2, n_3, etc are the number of moles of the component gases in the mixture.

n=Total number of gramme moles of the gas mixture.

$p_1=\frac{n_1}{n}P$; $p_2=\frac{n_2}{n}P$; $p_3=\frac{n_3}{n}P$,

$p_1=X_1P$; $p_2=X_2P$; $p_3=X_3P$.

Where X_1, X_2, X_3 are the mole fractions of the respective components.

(F) Application of Dalton's law of partial pressures (pressure of a moist gas) :

From this law we come to know that total pressure, exerted by the gas saturated with water vapour becomes equal to the actual pressure of the dry gas + the saturated vapour pressure of water (aqueous tension) at the temperature of the experiment. This saturated vapour pressure of water varies with temperature.

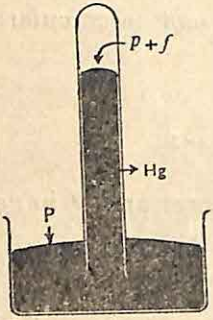

Fig. 1

Thus, the pressure of dry gas+aqueous-tension=barometric pressure.

or $p+f=P$, as height of mercury column stands stationary (Fig. 1).

or $p=P-f$. Where p, P and f, represent the pressure of dry gas, barometric pressure and aqueous tension expressed in cm. or mm. at the temperature of the experiment (t°C) respectively.

We have, $\frac{V_2\times P_2}{T_2}=\frac{V_1P_1}{T_1}$.

Here, $P_2=76$ cms ; $T_2=273°A$ (at N.T.P. or S.T.P.).

$P_1=P-f$.

$$\therefore \quad \frac{V_2\times 76}{273}=\frac{V_1\times(P-f)}{273+t}.$$

Solved problems

Boyle's Law :

1. A mass of hydrogen gas has a volume of 1,200 litres at a pressure of 1 atmosphere. To what value must the pressure be changed if the volume is to be reduced to 2 litres at the same temperature ? [*Jammu & Kashmir P. U.* '69]

We have from Boyle's law, $P_1V_1 = P_2V_2$.

$P_1 = 1$ atm ; $V_1 = 1{,}200$ litres ; $P_2 = ?$; $V_2 = 2$ litres.

$$\therefore \quad P_2 = \frac{P_1V_1}{V_2} = \frac{1 \times 1200}{2} = 600 \text{ atms.}$$

2. An air bubble is blown into a eudiometer tube 50 cm. long filled with mercury. If the volume of the air bubble before introduction was 0·5 ml., find its volume on reaching the top of mercury in the eudiometer. [Pressure of air = 750 mm. Hg ; Ignore the change in level of mercury on introducing air bubble.] [*Bihar H. S.* '63]

We have from Boyle's law,

$P_1V_1 = P_2V_2$; $P_1 = 75$ cms.,

$V_1 = 0{\cdot}5$ ml. ;

$P_2 = 75 - 50 = 25$ cms, ; $V_2 = ?$

$$\therefore \quad V_2 = \frac{P_1V_1}{P_2} = \frac{75 \times 0{\cdot}5}{25} = 1{\cdot}5 \text{ ml.}$$

This problem is worked out assuming temperature remaining same and ignoring the change in level of mercury on introducing air bubble.

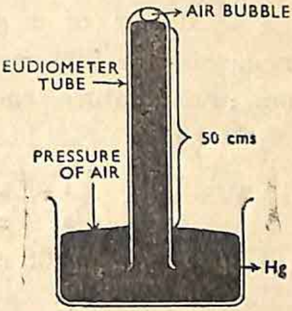

Fig. 2

3. An air bubble of volume 2·5 cc. is released at the bottom of a water tank of height 20 ft. Find its volume on reaching the surface of water in the tank.

[Pressure of air = 760 mm. Hg.]

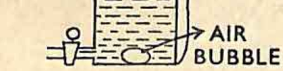

Fig. 3

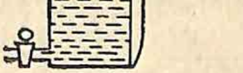

Fig. 4

We have from Boyle's law,

$P_1V_1 = P_2V_2$,

assuming temperature remaining same.

$V_1 = 2{\cdot}5$ cc.

P_1 = Pressure of air + pressure due to 20 ft. water column

$$= 76 + \frac{20 \times 12 \times 2{\cdot}54}{13{\cdot}6} = 120{\cdot}82 \text{ cms ; (vide. Fig. 3).}$$

$[\because \; 20 \text{ ft} = 20 \times 12 \times 2{\cdot}54 \text{ cms. ; } 12'' = 1' \text{ ; } 1'' = 2{\cdot}54 \text{ cms.}$

Conversion of height of water column into height of mercury column : $20 \times 12 \times 2{\cdot}54 \times d_1 = h_2 \times d_2$.

Here, d_1 = density of water in C. G. S. = 1 ; h = height of mercury column ; d_2 = density of mercury = 13·6.

$$\therefore \quad 20 \times 12 \times 2{\cdot}54 \times 1 = h_2 \times 13{\cdot}6 \; ; \; h_2 = \frac{20 \times 12 \times 2{\cdot}54}{13{\cdot}6}. \;]$$

$$P_2 = 76 \text{ cms} \; ; \; V_2'' = \; ? \quad V_2'' = \frac{P_1 V_1}{P_2} = \frac{120{\cdot}82 \times 2{\cdot}5}{76} = 3{\cdot}23 \text{ cc.}$$

4. 0·3 gm of a gas has 2205 cc. volume for movement of its molecules at 700 mm. pressure. If pressure is altered to 2205 mm ; temperature remaining constant, what would be the density of the gas ?

We have, $\frac{D_1}{D_2} = \frac{P_1}{P_2}$; $\quad D_1 = \frac{0{\cdot}3}{2205} = 0{\cdot}0001360$ gm. per cc ;

$D_2 = \; ?$ $\quad P_1 = 700$ mm ; $\quad P_2 = 2205$ mm.

$$\therefore \quad D_2 = \frac{P_2 D_1}{P_1} = \frac{2205 \times 0{\cdot}0001360}{700} = 0{\cdot}0004285 \text{ gm. per cc.}$$

∴ The density of the gas = 0·0004285 gm/cc.

Charles' Law

5. At what temperature in centigrade scale will the volume of a gas at 0°C double itself, pressure remaining constant ?

[**Uttar Pradesh Inter Board '67**]

We have from Charles' law, $\frac{V_1}{V_2} = \frac{T_1}{T_2}$; $T_2 = \frac{V_2 T_1}{V_1}$.

$V_1 = X$ cc (say) ; $T_1 = 273 + 0 = 273°$A ; $V_2 = 2X$ cc ; $T_2 = \; ?$

$T_2 = \frac{2X \; 273}{X} = 546°$A. Now, $T_2 = 273 + t_2 = 546$.

$\therefore \quad t_2 = 546 - 273 = 273°$C.

6. A gas expands from 1 litre to 1·128 litres due to a rise of temperature from 0°C to 35°C at constant pressure. From this, calculate the value of absolute zero (in centigrade scale).

[**W. Bengal H. S. '74**]

t_1 = temperature in centigrade scale at absolute zero.

For 35°C change in temperature (1·128 − 1) = 0·128 litre volume change, noted.

" 1°C " " " $\frac{0·128}{35}$ "

∴ " t_1°C " " " $\frac{0·128}{35} \times t_1$ "

At absolute zero, volume for the gas $= 1 + \frac{0·128 t_1}{35}$.

Now, $1 + \frac{0·128}{35} t_1 = 0$ ∵ At absolute zero, volume for the gas = 0.

∴ $t_1 = -273·5$°C.

7. An open vessel contains air at 27°C. To what temperature should the vessel be heated so that number of molecules in the vessel decreases by 75% ? Neglect the expansion of the vessel.

We have, $T_2 = \frac{T_1 D_1}{D_2}$. ∵ $\frac{D_2}{D_1} = \frac{T_1}{T_2}$.

$D_1 = \frac{100}{V}$; $T_1 = 273 + 27 = 300$°A.

[Where, number of molecules at 300°A = 100 ;
V = Volume of the vessel.]

When the vessel is heated, 75 molecules escape. The density of air becomes $D_2 = \frac{25}{V}$

$$= \frac{\frac{300 \times 100}{V}}{\frac{25}{V}} = 1200°\text{A}.$$

Gas equation

8. Spherical balloons of 21 cm. diameter are to be filled up with hydrogen at *S.T.P.* from cylinder containing the gas at 20 atmospheres and 27°C. If the cylinder can hold 2·82 liters of water, calculate the number of balloons that can be filled up.

[*W. Bengal. J. E. E.* '62 ; '70 ; *I. I. T.* '69.]

We have, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$; $P_1 = 20$ atm ;

$T_1 = 273 + 27 = 300$°A ;

$V_1=2{\cdot}82\times1000$ cc ; $P_2=1$ atm ; $T_2=273^\circ$A ; $V_2=n\times\frac{4}{3}\pi r^3$;
n = number of balloons ; r = radius of each balloon.

$$\frac{20\times2{\cdot}82\times1000}{300}=\frac{1\times n\times\frac{4}{3}\pi(10{\cdot}5)^3}{273}.$$

$$\therefore\ n=\frac{20\times2{\cdot}82\times1000\times273\times3\times7}{300\times4\times22\times(10{\cdot}5)^3}=10{\cdot}31\simeq10.$$

As the number should not be fraction, the number of balloons to be filled up at *S. T. P.* = 10.

Avogadro's hypothesis

9. A balloon of 200 litre capacity was filled completely with a gas having molecular weight, 4 at 650 mm. pressure and 25°C. Upon ascending, the temperature was found to be—79°C at a certain height, while the external pressure was decreased to 160 mm. What weight of the gas will have to be released to keep the balloon unburst ?

We have, $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$; $V_2=\frac{P_1V_1T_2}{T_1P_2}$.

$\because$ $P_1=650$ *mm* ; $V_1=200$ litres ; $T_1=273+25=298^\circ$K ;
$P_2=160$ *mm* ;
$T_2=273-79=194^\circ K$. $\therefore$ $V_2=\frac{650\times200\times194}{298\times160}$
$=528.94$ litres.

As the maximum capacity of the balloon is 200 litres, excess of the gas $(528{\cdot}94-200)=328{\cdot}94$ litres must be released. This volume of the gas is now converted into the volume at N.T.P. in order to get the weight of the gas released.

Now, $\frac{P_2V_2}{T_2}=\frac{P_0V_0}{T_0}$; $V_0=\frac{P_2V_2T_0}{T_2P_0}$

$$=\frac{160\times328{\cdot}94\times273}{194\times760}=97{\cdot}45 \text{ litres.}$$

$\because$ At N. T. P., $P_\circ=760$ *mm* ; $T_\circ=273^\circ K$.

We know 22·4 litre gas at N.T.P. weigh 1 *gm* mole = M *gm.* = 4 *gm.* $\because$ M = Molecular weight of the gas = 4.

$\therefore$ 97·45 litre gas at N. T. P. weigh $\frac{4\times97{\cdot}45}{22{\cdot}4}=17{\cdot}40$ *gms.*

The weight of the gas to be released = 17·40 gas.

Gas equation

10. A balloon of volume 280 *ml.* at 1 atmosphere pressure is pressed below the surface of ice-cold water (temperature 5°C) to a depth of 1000 cms. Calculate the volume of the balloon, if its initial temperature is 20°C.

We have, $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$; $V_2=\frac{P_1V_1T_2}{T_1P_2}$

$$=\frac{76\times280\times278}{293\times\left[76+\left(\frac{1000}{13{\cdot}6}\right)\right]}=135{\cdot}04\ ml.$$

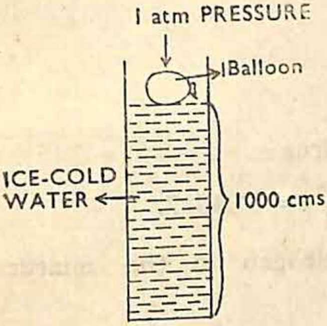

Fig. 5

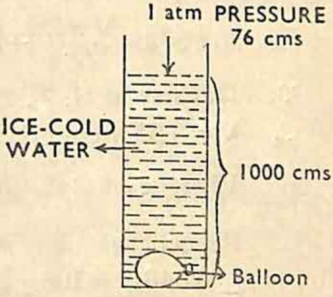

Fig. 6

Avogadro's hypothesis

11. A gaseous mixture contains nitrogen and hydrogen at 15°C and 700 *mm.* pressure. The density of the mixture is 0·6349 *gm* per litre. What is the percentage by weight of hydrogen in the mixture ? (N = 14 ; H = 1)

We have, $\frac{P_1D_2}{T_1}=\frac{P_2D_1}{T_2}$ $\therefore\ D_1=\frac{D_2T_2P_1}{P_2T_1}$.

Where, $D_1=?$ $D_2=0{\cdot}6349$ *gm*/litre ;

$P_1=760\ mm$; $T_2=273+15=288°K$;

$T_1=273°K$; $P_2=700\ mm.$

$$D_1=\frac{0{\cdot}6349\times288\times760}{700\times273}=0{\cdot}7272\ gm/\text{litre}.$$

The volume of nitrogen is assumed to be 'V' litre in the mixture. 22·4 litres of nitrogen at N. T. P. weigh 28 *gms.*

$\because$ 1 *gm.* mole. $N_2=28$ *gms.*

Molecular weight of nitrogen = 28.

$\therefore$ 'V' litre weighs $\left(\frac{V \times 28}{22{\cdot}4}\right)$ gm. N_2.

The volume of hydrogen = (1 − V) litre.

Again, 22·4 litres of hydrogen at N. T. P. weigh 2 *gms.*

$\because$ Molecular weight of hydrogen = 2.

$\therefore$ (1 − V) litre weighs $\frac{(1-V)\times 2}{22{\cdot}4}$ *gm.* H_2.

Weight of 1 litre mixture at N. T. P. = Density at N. T. P.

$$= \frac{V \times 28}{22{\cdot}4} + \frac{(1-V)\times 2}{22{\cdot}4}$$

Or $0{\cdot}7272 = \frac{V \times 28}{22{\cdot}4} + \frac{(1-V)\times 2}{22{\cdot}4}$

$\because$ Density at N. T. P. = 0·7272.

$\therefore$ V = 0·55 litre ; volume of hydrogen = 1 − 0·55 = 0·45 lit.

Weight of 0·45 litre $H_2 = \frac{0{\cdot}45 \times 2}{22{\cdot}4} = 0{\cdot}04017$.

Percentage by weight of hydrogen in the mixture

$$= \frac{0{\cdot}04017 \times 100}{0{\cdot}7272} = 5{\cdot}524.$$

Miscellaneous

12. Calculate the density of a gas at 102°C and 718 *mm.* pressure. The molecular weight of the gas is 40.

We have, $\frac{P_1}{D_1 T_1} = \frac{P_0}{D_0 T_0}$; $D_1 = \frac{P_1.D_0.T_0}{T_1.P_0}$.

$P_1 = 718\ mm$; $T_1 = 273 + 102 = 375°K$; $D_1 = ?$

$P_0 = 760\ mm$; $T_0 = 273°K$; $D_0 = 1{\cdot}786$ *gm.*/litre

$\because$ $D_0 = \frac{40}{22{\cdot}4} = 1.786.$

$\therefore$ $D_1 = \frac{718 \times 1{\cdot}786 \times 273}{375 \times 760} = 1{\cdot}228$ gms. per litre.

$\therefore$ Density of the gas = 1·228 gms. per litre.

Avogadro's hypothesis

13. Core of the Sun is made up of gases with average molecular weight = 2. Their density and pressure are 1·3 gm/cc.

and $1{\cdot}12\times10^9$ atmosphere respectively. Calculate the temperature of the sun. [*I. I. T. (Group A) '66.*]

We have, 22400 cc of gases in the sun at N. T. P. weigh 2gms, according to Avogadro's hypothesis.

$$D_0=\frac{2}{22400}\text{ gm. per c.c.}$$

Again, $\dfrac{P_0}{D_0T_0}=\dfrac{P_1}{D_1T_1}$; $T_1=\dfrac{P_1D_0T_0}{P_0D_1}$.

$T_0=273°K$; $P_0=1$ atm ; $P_1=1{\cdot}12\times10^9$ atms ;

$D_1=1{\cdot}3$ gm. per cc.

$$T_1=\frac{1{\cdot}12\times10^9\times\frac{2}{22400}\times273}{1\times1{\cdot}3}=(2{\cdot}1\times10^7)°A\text{ or}K.$$

Ideal gas equation

14. 2 moles of oxygen have 1850 cc. space for movement of its molecules at—50°C and 1580 mm. pressure. How many moles of chlorine would require 1000 cc. space at 27°C and 790 mm. pressure?

We have, $P_1V_1=n_1RT_1$; $R=\dfrac{P_1V_1}{n_1T_1}$ for oxygen.

[R=molar gas constant.]

And $R=\dfrac{P_2V_2}{n_2T_2}$for chlorine $\therefore$ $\dfrac{P_1V_1}{n_1T_1}=\dfrac{P_2V_2}{n_2T_2}$.

$$n_2=\frac{n_1T_1\times P_2V_2}{P_1V_1\times T_2}=\frac{2\times223\times790\times1000}{1580\times1850\times300}=0{\cdot}4017.$$

$\because$ $P_1=1580$ mm ; $T_1=273-50=223°K$; $V_1=1850$ cc., $n_1=2$ moles ;

$P_2=790$ mm ; $T_2=273+27=300°K$; $V_2=1000$ cc ; $n_2=?$

$\therefore$ Number of moles of chlorine $=0{\cdot}4017$.

Avogadro's number

15. A closed vessel containing carbon tetrachloride vapour is evacuated to 0·0076 mm. of Hg at 0°C. Calculate the number of molecules per milli litre at this pressure.

We have, $PV=nRT$; $\dfrac{0{\cdot}0076}{760}\times\dfrac{1}{1000}=n\times0{\cdot}0821\times273.$

$\because$ 1 milli litre (ml) $= \frac{1}{1000}$ litre.

$$n = \frac{0{\cdot}0076}{1000 \times 760 \times 0{\cdot}0821 \times 273} \text{ gm. moles.}$$

$\because$ 1 gm mole $= 6{\cdot}023 \times 10^{23}$ molecules $=$ Avogadro's number.

$$\therefore \text{ Number of molecules} = \frac{0{\cdot}0076 \times 6{\cdot}023 \times 10^{23}}{1000 \times 760 \times 0{\cdot}0821 \times 273}$$

$$= 26{\cdot}87 \times 10^{9} \backsimeq 27 \times 10^{9}.$$

Ideal Gas equation

16. A small glass bottle weighed 5·014 gm. empty. Filled with a pure saturated organic liquid. The sealed bottle weighed 5·284 gms. The bottle was broken in a vessel that was jacketed by a bath of water that boiled at 99·8°C. The initial mercury level in the gas burette was 10·46 cc, and the final level was 46·22 cc. The barometric pressure was constant at 754·6 mm. Hg, and the temperature of the laboratory was 23·2°C. Find its molecular weight as it exists at 99·8°C.

$$\text{We have, } PV = \frac{W}{M} RT\text{ ; } M = \frac{WRT}{PV}\cdot$$

$W = 5{\cdot}284 - 5{\cdot}014 = 0{\cdot}270$ gm ; $T = 273 + 23{\cdot}2 = 296{\cdot}2°$A ,

$V = 46{\cdot}22 - 10{\cdot}46 = 35{\cdot}76$ cc $= 0{\cdot}03576$ litre ;

$$P = \frac{754{\cdot}6}{760} \text{ atm ; } M = \frac{0{\cdot}270 \times 0{\cdot}0821 \times 296{\cdot}2}{\frac{754{\cdot}6}{760} \times 0{\cdot}03576} = 185.$$

$\because$ $R = 0{\cdot}0821$ lit. atm. per degree per mole.

17. Find the density of 4·3 gms. of hydrogen at 25°C and 770 mm. pressure.

$$\text{We have, } P = \frac{D}{M} RT\text{ ; } D = \frac{PM}{RT}$$

$$= \frac{\frac{770}{760} \times 2}{0{\cdot}0821 \times (273 + 25)} = 0{\cdot}08283 \text{ gm lit}^{-1} \text{ at } 25°\text{C}.$$

Dalton's law of partial pressures

18. 400 ml. of oxygen at 700 mm. pressure and 300 ml. of nitrogen at 800 mm. pressure were mixed in a one litre flask, the

temperature being constant. Calculate the total pressure of the mixture. [*Poona P.U.* '67.]

We have, $p_1v_1 = n_1RT_1$;

$$n_1 = \frac{p_1v_1}{RT_1} = \frac{\frac{700}{760} \times \frac{400}{1000}}{0{\cdot}0821 \times T_1} = \frac{0{\cdot}3684}{0{\cdot}0821T_1}.$$

$p_2v_2 = n_2RT_2$;

$$n_2 = \frac{p_2v_2}{RT_1} = \frac{\frac{800}{760} \times \frac{300}{1000}}{0{\cdot}0821\ T_1} = \frac{0{\cdot}3158}{0{\cdot}0821T_1} \quad \because \quad T_1 = T_2.$$

Now, $p_1 = \frac{n_1}{n_1+n_2} P$; $P = \frac{n_1+n_2}{n_1} p_1$

$$= \frac{\frac{0{\cdot}3684}{0{\cdot}0821T_1} + \frac{0{\cdot}3158}{0{\cdot}0821T_1}}{\frac{0{\cdot}3684}{0{\cdot}0821T_1}} p_1$$

or $P = \frac{0{\cdot}3684 + 0{\cdot}3158}{0{\cdot}3684} p_1 = 1{\cdot}858\ p_1.$

Again, $p_1 \times 1 = \frac{0{\cdot}3684}{0{\cdot}0821T_1} \times 0{\cdot}0821 \times T_1 = 0{\cdot}3684.$

$\therefore \quad P = 1{\cdot}858 \times 0{\cdot}3684 \text{ atm} = 1{\cdot}858 \times 0{\cdot}3684 \times 760 = 520{\cdot}10 \text{ mm}.$

19. Air contains 79% N_2 and 21% O_2 by volume. Find the mole fraction of each gas in air.

At constant temperature and pressure, volumes required for movement of gas molecules are directly proportional to the number of moles of gases. Hence we can write number of moles of nitrogen ∝ volume of nitrogen gas molecules ; number of moles of oxygen ∝ volume of oxygen.

$$\text{Mole fraction of } N_2 = \frac{\text{Number of moles of nitrogen}}{\text{Total number of moles of } N_2 \text{ and } O_2}$$

$$= \frac{\text{Volume of } N_2}{\text{Total volume}} = \frac{79}{100} = 0{\cdot}79.$$

$$\text{Similarly, Mole fraction of } O_2 = \frac{\text{Volume of } O_2}{\text{Total volume}} = \frac{21}{100} = 0{\cdot}21.$$

20. Find the composition of a gaseous mixture containing nitrogen, oxygen and argon which exerts a pressure of 1500 mm.

at 27°C. The partial pressures of oxygen and argon are respectively 300 and 90 mm.

We have from the Dalton's law of partial pressures,

partial pressure = mole fraction × total pressure.

$$\therefore \quad \text{Mole fraction} = \frac{\text{Partial pressure}}{\text{Total pressure}}.$$

$$\text{Mole fraction of oxygen} = \frac{300}{1500} = 0{\cdot}20.$$

$$\text{Mole fraction of argon} = \frac{690}{1500} = 0{\cdot}46.$$

$\because$ Mole fraction of Oxygan + Mole fraction of Argon + mole fraction of Nitrogen = 1.

or $0{\cdot}2 + 0{\cdot}46$ + mole fraction of Nitrogen = 1

or $0{\cdot}66$ + mole fraction of Nitrogen = 1

or Mole fraction of nitrogen $= 1 - 0{\cdot}66 = 0{\cdot}34$.

The volume of the mixture is assumed to be 100cc.

$$\text{Now, mole fraction} = \frac{\text{volume of the gas}}{\text{total volume}}.$$

Volume of oxygen $= 0{\cdot}20 \times 100 = 20$cc.

Volume of argon $= 0{\cdot}46 \times 100 = 46$cc.

Volume of nitrogen $= 0{\cdot}34 \times 100 = 34$ cc.

$\therefore$ Composition of the mixture by volume is 20%O_2 ; 46%Ar & 34%N_2.

Gas equation :

21. A metallic cylinder of capacity 480 ml. containing nitrogen gas at 700 mm. and 17°C is connected to another cylinder of capacity 300 ml. and containing oxygen gas at 650 mm. pressure. What is the total pressure of the mixture ?

We have, pressure of the mixture = partial pressure of nitrogen + partial pressure of oxygen.

Total volume of the mixture = 480 + 300 = 780 ml.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \because \quad T_1 = T_2 \text{ (say)} \quad \therefore \quad P_1V_1 = P_2V_2.$$

Where, P_1 = pressure of nitrogen = 700 mm. ; $V_1 = 480$ ml. ; before connection.

p_2 = partial pressure of nitrogen in the mixture = ?

$$V_2 = 780 \text{ ml.} \quad \therefore \quad p_2 = \frac{P_1 V_1}{V_2} = \frac{700 \times 480}{780} = 430{\cdot}7 \text{ mm.}$$

Again, $P_3 V_3 = p_3 . V_2$

$$\therefore \quad p_3 = \frac{P_3 V_3}{V_2} = \frac{650 \times 300}{780} = 250 \text{ mm.}$$

$\because$ P_3 = pressure of oxygen before connection = 650 mm. ;
V_3 = volume of oxygen " " = 300 ml. ;
p_3 = partial pressure of oxygen in the mixture = ?
V_2 = 780 ml. = total volume of the mixture.

Pressure of the mixture $= p_2 + p_3 = 430{\cdot}7 + 250 = 680{\cdot}7$ mm.

Application of Dalton's law of partial pressure :

22. A certain quantity of nitrogen occupies 150 cc. when collected over water at 15°C and 750 mm. pressure. If it occupied 138 cc. in dry state at N.T.P., calculate the pressure of water vapour at 15°C (aqueous tension).

We have, $\frac{P_1 V_1}{T_1} = \frac{P_0 V_0}{T_0}$; P_1 = pressure of dry gas.

Now, atmospheric pressure
= pressure of dry gas + pressure of water vapour (aqueous tension).

$750 = P_1 + f$; $P_1 = 750 - f$; $V_1 = 150$ cc. ; $T_1 = 273 + 15 = 288°A$.
$P_0 = 760$ mm. ;
$V_0 = 138$ cc. ;
$T_0 = 273°$ K.

$$\because \quad \frac{(750 - f) \times 150}{288} = \frac{760 \times 138}{273} \quad \therefore \quad f = 12{\cdot}5 \text{ mm.}$$

Miscellaneous :

23. The density of air is 1·172 gm. per litre at 27°C and 1 atm. If it is assumed that air contains only oxygen and nitrogen, what is the percentage composition by volume of air ?

Let 100 cc. of air contain "V" cc. of oxygen and (100 − V) cc. of nitrogen at 27°C.

22400 cc. of oxygen at N.T.P. weigh 32 gms.

Now, $\frac{22400 \times 760}{273} = \frac{V_1 \times 760}{273 + 27}$.

$\therefore$ $V_1 = 24610$ cc. = volume of oxygen at 27°C.

24610 cc. of oxygen at 27°C weigh 32 gms.

$\therefore$ V cc. " " " " " $\frac{32}{24610} \times V$ gms.

$= 0{\cdot}0013V$ gms.

Similarly, 24610 cc. of nitrogen at 27°C weigh 28 gms.

$\therefore$ $(100 - V)$ cc. " " " " $\frac{28}{24610} \times (100 - V)$ gms.

$= 0{\cdot}001138(100 - V)$ gms.

Now, weight of 100 cc. of air at 27°C
$= 0{\cdot}0013\,V + 0{\cdot}001138(100 - V)$.

$\therefore$ Weight of 1 cc. of air at 27°C
$= \frac{0{\cdot}0013\,V + 0{\cdot}001138(100 - V)}{100}$.

$\because$ Density of air at 27°C = 1·172 gm./litre.

$\therefore$ Weight of 1 cc. of air at 27°C $= \frac{1{\cdot}172}{1000} = 0{\cdot}001172$.

$\because$ $0{\cdot}001172 = \frac{0.0013\,V + 0{\cdot}001138(100 - V)}{100}$ $\therefore$ $V = 21$ cc.

Volume of nitrogen = (100 − 21) cc. = 79 cc.

$\therefore$ Volume percentages of oxygen and nitrogen are 21 and 79 respectively.

24. A four-litre glass vessel contains oxygen and nitrogen in equimolecular proportions at a pressure of 100 mm. Find the density of the mixture at 27°C.

As the gases in the mixture are present in equimolecular proportion, the pressure exerted by both the gases will be equal. The pressure of the mixture is the sum of the partial pressures of the gases.

100 = partial pressure of oxygen + partial pressure of nitrogen
= partial pressure of oxygen + partial pressure of oxygen.

∵ Partial pressure of nitrogen = partial pressure of oxygen.

or 100 = 2 × partial pressure of oxygen.

∴ Partial pressure of oxygen $= \frac{100}{2} = 50$ mm.

and partial pressure of nitrogen = 50 mm.

Density of oxygen at N.T.P $= \frac{32}{22400} = 0.001430$.

Density of nitrogen at N.T.P. $= \frac{28}{22400} = 0.001250$.

For oxygen, density at 27°C $= \frac{0{\cdot}001430 \times 273 \times 50}{760 \times 300}$

$= 8{\cdot}563 \times 10^{-5}$ gm./cc.

∵ $\frac{P_1}{D_1 T_1} = \frac{P_0}{D_0 T_0}$; $D_1 = \frac{D_0 T_0 P_1}{P_0 T_1}$;

$D_0 = 0{\cdot}001430$; $T_0 = 273$; $P_0 = 760$; $P_1 = 50$ mm. ;

$T_1 = 273 + 27 = 300°K$.

For nitrogen, density at 27°C $= \frac{0{\cdot}001250 \times 273 \times 50}{760 \times 300}$

$= 7{\cdot}485 \times 10^{-5}$ gm. per cc.

∴ Density of the mixture at 27°C $= 8{\cdot}563 \times 10^{-5} + 7{\cdot}485 \times 10^{-5}$

$= 1{\cdot}6 \times 10^{-4}$ gm. per cc.

Avogadro's hypothesis and molar concept :

25. Find the volume occupied by one molecule of water.
[Density of water = 1 gm. per cc.]
Mol. wt. of $H_2O = 18$; $N = 6{\cdot}023 \times 10^{23}$.

1 gm. mole. water = 18 gms. of water.

∵ Molecular weight of water = 18.

∵ 1 gm. water occupies 1 cc. volume.

∴ 18 gm. water will occupy 18 cc.

∵ 1 gm. mole water contains $6{\cdot}023 \times 10^{23}$ molecules

∴ $6{\cdot}023 \times 10^{23}$ number of molecules will occupy 18 cc.

∴ 1 molecule of water will occupy $= \frac{18}{6{\cdot}023 \times 10^{23}}$

$= 2{\cdot}96 \times 10^{-23}$ cc.

Miscellaneous :

26. A cylinder of capacity 10 litres contains hydrogen gas at 60 atm. and 25°C. What will be the density of hydrogen in the cylinder ?

We have, $\frac{P_1V_1}{T_1}=\frac{P_0V_0}{T_0}$.

$\therefore\ V_0=\frac{P_1V_1T_0}{T_1P_0}=\frac{60\times10\times273}{298\times1}=549{\cdot}8$ litres.

We know at N.T.P. 22·4 litre hydrogen weigh 2 gms.

$\therefore$ at N.T.P. 549·8 litre hydrogen weigh $\frac{2\times549{\cdot}8}{22{\cdot}4}=49{\cdot}09$ gm.

Density of hydrogen in the cylinder at 25°C and 60 atm.

$$=\frac{\text{wt. of hydrogen}}{\text{volume of the cylinder}}=\frac{49{\cdot}09}{10}=4{\cdot}909 \text{ gms. per litre.}$$

$\because$ mass of the gas is fixed. $\therefore$ weight of hydrogen at N.T.P. = weight of hydrogen at 25°C and 60 atm.

27. A gas occupies 400 cc. at 0°C and 560 mm. of Hg. If the same gas occupies 680 cc. at 25°C, what pressure would benzene manometer read at this temperature ?
(Density of benzene is 0·87 gm. per cc. at this temperature)

We have, $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$.

P_1 = height of mercury column
= 56 cms. of mercury column
= $56\times15{\cdot}63$ cm. benzene column (see bottom) ;
$V_1=400$ cc. ; $T_1=273°A$;
$P_2=?$ $V_2=680$ cc. ; $T_2=273+25=298°A$.

$$P_2=\frac{P_1V_1T_2}{T_1V_2}=\frac{56\times15{\cdot}63\times400\times298}{273\times680}=561{\cdot}9 \text{ cms.}$$

$\therefore$ height of benzene in the manometer = 561·9 cms.
$\because$ $h_1\times\rho_1\times g=h_2\times\rho_2\times g$.
Where, h_1 = height of mercury column ;
ρ_1 = density of mercury ;

g = acceleration due to gravity ;
h_2 = height of the benzene column ;
p_2 = density of benzene.

$$\therefore \quad h_2 = \frac{h_1 \times \rho_1}{\rho_2} = \frac{56 \times 13{\cdot}6}{0{\cdot}87} = 56 \times 15{\cdot}63 \text{ cms.}$$

28. A balloon has a volume of 480 cc. at 5°C. The balloon is swelled up to 7/8 of its maximum streching capacity. Will it burst if brought into a room temperature at 20°C ? What is the maximum temperature above which it will burst ?

We have, $\frac{7}{8} \times$ streching capacity $= 480$ cc.

$\therefore$ streching capacity $= \frac{8}{7} \times 480 = 548{\cdot}6$ cc.

$$\text{Now, } \frac{V_1}{V_2} = \frac{T_1}{T_2} \text{ (pressure is kept constant) ; } V_2 = \frac{T_2}{T_1} V_1$$

$$= \frac{293 \times 480}{278} = 505{\cdot}9 \text{ cc.}$$

$\because \quad V_1 = 480$ cc ; $T_1 = 278^\circ A$; $T_2 = 293^\circ A$: $V_2 = ?$

Since the volume of the balloon becomes 505·9 cc. at 20°C, it will not burst because its maximum volume could be 505·9 cc.

$$\text{Now, } T_2 = \frac{T_1 V_2}{V_1} = \frac{278 \times 548{\cdot}6}{480} = 317{\cdot}8^\circ A = 44{\cdot}8^\circ C.$$

29. An open vessel at a temperature of 10°C is heated at constant pressure to 400°C. What fraction of the weight of air originally contained in the vessel is expelled ?

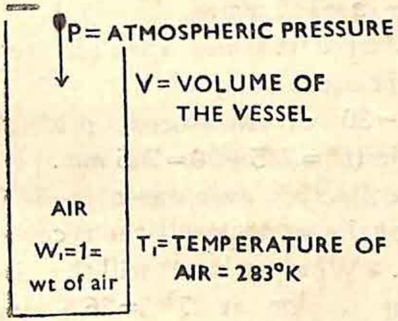

Fig. 7

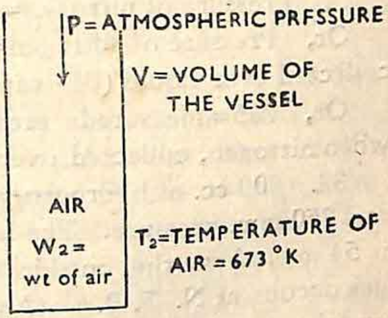

Fig. 8

$W_2 = 1 - x$. Where, x = fractional amount of air expelled.

$$\text{We have, } PV=\frac{W}{M}RT\ ;\quad T=\frac{PVM}{R}\cdot\frac{1}{W}=\text{constant}.\frac{1}{W}$$

$$T\propto\frac{1}{W}\quad\therefore\quad\frac{T_2}{T_1}=\frac{W_1}{W_2}\ ;\ \frac{673}{283}=\frac{1}{1-x}\quad\therefore\quad x=0{\cdot}579.$$

30. A gas cylinder containing cooking gas can withstand a pressure of 14·9 atmospheres. The pressure gauge of the cylinder indicates 12 atmospheres at 27°C. Due to a sudden fire in the building, its temperature starts rising. At what temperature the cylinder will explode ? [*I.I.T.* (*Group B*) *'75*].

Volume of the cylinder is fixed. We can use the expression,

$$\frac{P_1}{T_1}=\frac{P_2}{T_2}\ ;\ V_1=V_2=\text{volume of the cylinder.}$$

$$P_1=12\text{ atm}\ ;\ T_1=273+27=300^\circ A\ ;\ P_2=14{\cdot}9\text{ atm}\ ;\ T_2=?$$

$$T_2=\frac{P_2T_1}{P_1}=\frac{14{\cdot}9\times300}{12}=372{\cdot}5^\circ A=99{\cdot}5^\circ\text{C}.$$

Application of Dalton's law of partial pressures :

31. At 25°C a certain amount of nitrogen was collected over a liquid (A). Its observed vapour pressure was 750 mm. If the same amount of nitrogen is collected over a liquid (B) at 25°C, what would be the measured pressure ? Vapour pressures of liquid (A) and (B) are 15 mm. and 30 mm. respectively at 25°C. [*Sardar Patel* P.U. '67].

P = 750 mm. = pressure of nitrogen + pressure of liquid (A) vapour.

∴ Pressure of nitrogen = 750 − 15 = 735 mm.

Or, Pressure of nitrogen = measured pressure when nitrogen, collected over liquid (B) − vapour pressure of liquid (B).

Or, 735 = measured pressure − 30 ∴ Measured pressure when nitrogen, collected over liquid (B) = 735 + 30 = 765 mm.

32. 200 cc. of hydrogen were collected over water at 27°C and 750 mm. pressure. The level of the water inside the receiver is 54 mm. above the outside level. What volume will the dry gas occupy at N. T. P. ? (Aqueous tension at 27°C = 26·5 mm. and density of mercury = 13·6).

Atmospheric pressure = pressure of dry gas + aqueous tension.

Or, Pressure of dry gas = Atmospheric pressure − Aqueous tension.

Or, Pressure of dry gas $=75-\frac{5\cdot4}{13\cdot6}-2\cdot65=71\cdot95$ cms.

[Vide. Problems 2 & 3.]

We have, $\frac{P_1V_1}{T_1}=\frac{P_\circ V_\circ}{T_\circ}$ ∴ $V_\circ=\frac{P_1V_1T_\circ}{P_\circ T_1}$

$$=\frac{71\cdot95\times200\times273}{76\times300}=172\cdot3 \text{ cc.}$$

Molecular weight :

33. On heating strongly 0·406 gm. of potassium chlorate, 139 cc. of oxygen were obtained and potassium chloride remaining weighed 0·247 gm. The oxygen was measured over water at a temperature of 27°C and 71·14 cms. Find the molecular weight of oxygen which may be deduced from these data. (Aqueous tension at 27°C = 2·66 cms.)

We have, $PV=\frac{W}{M}RT$; $P=71\cdot14-2\cdot66=68\cdot48$ cms ;

$V=139$ cc ; $T=300^\circ A$; W = wt. of oxygen $=0\cdot406-0\cdot247$
$=0\cdot159$ gm.

∵ Weight of potassium chlorate = wt. of potassium chloride + wt. of oxygen. ∴ $\frac{68\cdot48}{76}\times\frac{139}{1000}=\frac{0\cdot159}{M}\times0\cdot0821\times300$;

$$M=\frac{0\cdot159\times8\cdot21\times3\times76}{68\cdot48\times0\cdot139}=31\cdot26.$$

Gas equation :

34. Two spherical vessels contain equal quantities of air. The temperature of one is 239°C and that of the other 456°C. If the internal radius of the first is 8 cms. and that of the other 9 cms ; show that the pressures of air inside both are equal.

We have, $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$; $\frac{P_1\times\frac{4}{3}\pi(8)^3}{273+239}=\frac{P_2\times\frac{4}{3}\pi(9)^3}{273+456}$.

∴ $\frac{P_1}{P_2}=1$ Or, $P_1=P_2$.

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Boyle's law :

35. Mercury is poured into a tube closed at one end until it reaches a point 2·5 cms. from the open end. The tube is then inverted and placed in a vertical position with the lower end in a trough of mercury. It is then found that air fills 38 cms. of the tube while a column of mercury 70 cm. long is sustained below it. Find the atmospheric pressure.

P = Atmospheric pressure ; a = Area of cross section of the tube. According to the question, $2{\cdot}5a$ cc. air has already entered the tube. This volume of air, on inversion of the tube over trough of mercury, gets expanded to $38a$ cc. volume. Let the pressure of this expanded air $= P_1$.

Now, $PV = P_1V_1$; temperature is supposed to be constant.

$$P \times 2{\cdot}5a = P_1 \; 38a \; ; \; P_1 = \frac{2{\cdot}5}{38} P.$$

$$P = \text{Atmospheric pressure} = P_1 + 70 = \frac{2{\cdot}5}{38} P + 70.$$

$$\text{Or, } \; P - \frac{2{\cdot}5}{38} P = 70 \quad \therefore \quad P = 74{\cdot}9 \text{ cm. Hg.}$$

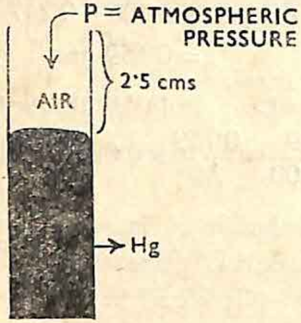


Fig. 9

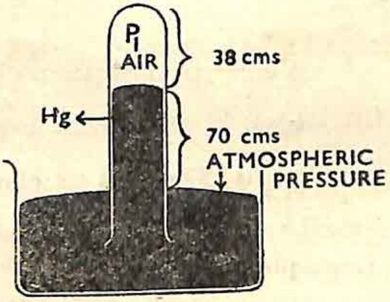


Fig. 10

36. A cylinder contains 100 litres of a gas at 5 atm. pressure. A quantity of the gas is taken out from the cylinder and it is found that the volume of the gas taken out occupies 40 litres at one atm. pressure. Find the pressure of the residual gas in the cylinder ; assuming temperature remaining constant throughout the interval.

$$P_1V_1=P_2V_2\ ;\quad 5\times100=1\times V_2\ ;\ V_2=500 \text{ litres.}$$

At 1 atm. pressure, volume of residual gas $=500-40$
$=460$ litres.

As volume of the cylinder becomes 100 litres,

$$1\times460=P_3.100 \quad \therefore \quad P_3=\frac{460}{100}=4{\cdot}6 \text{ atm}\ ;\quad P_3=\text{pressure}$$

of the residual gas in the cylinder.

Ideal gas equation :

37. The capacities of two cylinders are in the ratio of 3 : 1. They communicate through a connecting pipe. The stop-cock of the pipe is closed and the two cylinders are filled with sulphur dioxide gas, the larger one at a pressure of 8 atms. and the smaller one at a pressure of 4 atms. If the stop—cock is opened to allow free flow of the gas, what will be the final pressure within the cylinders ?

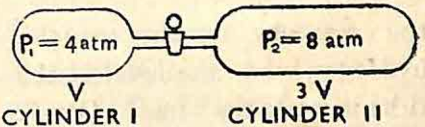


Fig. 11

For Cylinder I,
$P_1V_1=n_1RT$;
$4.V=n_1RT \quad \ldots \quad \ldots \quad$ (i)
For cylinder II,
$P_2V_2=n_2RT$;
$8.3V=n_2RT \quad \ldots \quad \ldots \quad$ (ii)

T is the temperature of sulphur dioxide gas, assumed to remain constant, n_1 and n_2 become numbers of moles of sulphur dioxide in cylinder I and II respectively. R is the universal molar gas constant. Sulphur dioxide is supposed to behave ideally.

Dividing equation (i) by (ii),

$$\frac{4\,V}{24.V}=\frac{n_1RT}{n_2RT};\ \frac{1}{6}=\frac{n_1}{n_2}\ ;\ n_2=6n_1.$$

After the opening the stop-cock, $P(3V+V)=(n_1+n_2)RT$.

[Where, P = final pressure within the cylinders ; total volume of the cylinders, neglecting the space between the two cylinders $=V_1+V_2=V+3V$; n = total number of moles of sulphur dioxide $=n_1+n_2$.]

Or, $P.4V=(n_1+6n_1)RT$ ...(iii) Dividing equation (iii) by (i),

$$\frac{P.4V}{4.V}=\frac{(n_1+6n_1)RT}{n_1RT}\ ;\quad P=\left(\frac{n_1}{n_1}+\frac{6n_1}{n_1}\right)=1+6=7 \text{ atms.}$$

Boyle's law :

38. 100 cc. of hydrogen are collected by the displacement of mercury, the level of which is found after the collection of the gas to stand at a height of 20 cms. above that of the mercury in the trough. Calculate the volume of the hydrogen when the level of the mercury inside and outside the tube is made the same. [P=76 cms.]

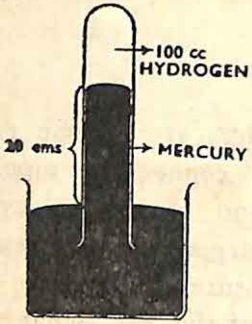


Fig. 12

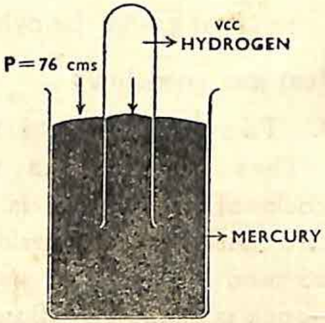


Fig 13

$100 \times (76-20) = V.76$

[Vide. $V_1P_1 = V_2P_2$; at constant temperature]

$V_1 = 100$ cc ; $P_1 = (76-20)$ cms ;

$V_2 = V$ cc ; $P_2 = 76$ cms = pressure of atmosphere = pressure of hydrogen (Fig. 13).

Or, $100 \times 56 = V.76$

Or, $V = \frac{100 \times 56}{76} = 73{\cdot}68$ cc.

Boyle's law :

39. A cylinder contains 30 litre air at 50 atms. If a leak is produced in the cylinder, calculate the volume of air which will escape into atmosphere.

$P_1V_1 = P_2V_2$ [T is kept constant] ; $50 \times 30 = 1 \times V_2$;

$V_2 = 1500$lits.

∴ Volume of air escaping into atmosphere $= 1500 - 30$

$= 1470$ lits.

40. Two cylinders of 150 litre capacity each, are filled with air, one at a pressure of 15 atms. and the other at a pressure of 10 atms. If the cylinders are connected with a pipe, calculate the mass of air, transferred from one cylinder to another at 0°C ? [Density of air at N.T.P. = 1·22 gms./litre]

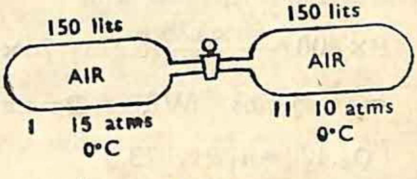


Fig. 14

$\frac{P_1}{P_2}=\frac{D_1}{D_2}$, at constant temperature.

For cylinder I, $\frac{1}{15}=\frac{1{\cdot}22}{D_2}$; $D_2=1{\cdot}22\times 15$ gms./lit.

D_2 = density of air at 15 atms and 0°C.

For cylinder II, $\frac{1}{10}=\frac{1{\cdot}22}{D_3}$; $D_3=1{\cdot}22\times 10$ gms /lit.

D_3 = density of air at 10 atms. and 0°C.

W_1 = amount of air in I = $1{\cdot}22\times 15\times 150$ gms.

W_2 = " " " " II = $1{\cdot}22\times 10\times 150$ gms.

W_1-W_2 = difference in amounts = $1{\cdot}22\times 15\times 150 - 1{\cdot}22\times 10\times 150 = 1{\cdot}22\times 150(15-10)$

$= 1{\cdot}22\times 150\times 5 = 915$ gms.

As both of the cylinders have the same volume (150 lits.), an equal amount of air shall remain present in each of the cylinder and therefore equal amount of air shall be distributed in between the two cylinders.

∴ Mass of air, transferred from the cylinder I to II $=\frac{915}{2}$

$= 457{\cdot}5$ gms.

Ideal gas equation :

41. 100 cc. oxygen and 75 cc. of hydrogen, both measured at N.T.P., are mixed together and allowed to expand to a volume of 400 cc. at 0°C. What is the total pressure of the mixture ? Calculate the partial pressures of oxygen and hydrogen.

$100\times 76=n_1R\times 273$ ... (i)

$75\times 76=n_2R\times 273$ ... (ii)

$P\times 400=(n_1+n_2)R\times 273$ ... (iii)

Adding equation i) and (ii), $100\times 76+75\times 76$

$$=n_1R\;273+n_2R\;273$$

or, $76(100+75)=273R(n_1+n_2)$

or, $n_1+n_2=\dfrac{76\times 175}{273R}$. On substitution the value of (n_1+n_2) in equation (iii),

$$P\times 400=\frac{76\times 175}{273R}R\;273=76\times 175 \quad \text{or,} \quad P=\frac{76\times 175}{400}$$

$=32{\cdot}25$ cms. Where, $P=$ total pressure of the mixture.

$p_{O_2}.400=n_1R\times 273.$

From equation (i) $n_1R=\dfrac{100\times 76}{273}$

$$\therefore \quad p_{O_2}.400=\frac{100\times 76}{273}\times 273=100\times 76\;;$$

$$p_{O_2}\times 4=76\;;\; p_{O_2}=19 \text{ cms.}$$

$$\therefore \quad p_{H_2}=32{\cdot}25-19=13{\cdot}25 \text{ cms.}$$

Molecular weight :

42. When 10 gms. of a solid are heated, the residue weighs 5·6 gms. and 2·24 litres of a gas are evolved at N.T.P. Calculate the molecular weight of the gas. [*Ranchi University, 1973.*]

Amount of gas evolved $=10-5{\cdot}6=4{\cdot}4$ gms ; $P=1$ atm ;
$V=2{\cdot}24$ lits. ; $T=273^\circ A$; $R=0{\cdot}0821$ lit. atm. per deg per mole.

We have, $PV=\dfrac{W}{M}RT$; $1\times 2{\cdot}24=\dfrac{4{\cdot}4}{M}\,0{\cdot}0821\times 273$;

or, $M=\dfrac{4{\cdot}4\times 0{\cdot}0821\times 273}{2{\cdot}24}=44{\cdot}03.$

*N.B. Log calculation must be at the right hand side *w.r.t.* procedure of sum. Without this no mark shall be given. Students are asked to show mathematical calculations at the right hand side of the page.

Gas equation :

43. 50 cc. of nitrogen gas at N.T.P. are confined in a tube of cross section 1·2 sq. cms. and standing in a trough of mercury

the column of which stands at a height of 15 cms. The pressure is now changed to 75 cms. and the temperature to 31°C. Find the length of column of tube containing nitrogen.

We have, $\frac{50\times 76}{273}=\frac{V_1(76-15)}{273}$; $V_1=\frac{50\times 76}{61}$ cc.

Now, $\frac{(76-15)V_1}{273}=\frac{75\times V_2}{304}$ or, $\frac{61\times 50\times 76}{61\times 273}=\frac{75\times V_2}{304}$

or, $V_2=\frac{50\times 76\times 304}{273\times 75}$ cc. $\therefore\ l=\frac{V_2}{1{\cdot}2}=\frac{50\times 76\times 304}{273\times 75\times 1{\cdot}2}=47{\cdot}01$ cms

Where, V_1 = volume of nitrogen when mercury column stands at a height of 15 cms at 0°C(273°A) ; V_2 = volume of the gas at 75 cm. pressure and at 31°C ; l = the length of column of the tube containing nitrogen.

Avogadro's hypothesis and molar concept :

44. Calculate density of a mixture at N.T.P. which contains two gases *A* and *B*, with molecular weights respectively 60 and 40, in the proportion 1 : 4 by volume.

22400 cc. of *A* gas at N.T.P. weigh 60 gms.

V cc. „ „ „ „ „ „ $\frac{60\times V}{22400}$ gms.

∵ 1 gm. mole of $A=60$ gms.

Where, V is assumed to be volume of *A* gas at N.T.P.

Now, 4V cc. of *B* gas at N.T.P weigh $=\frac{40\times 4V}{22400}$ gms.

Density of the mixture at N.T.P. = density of A at N.T.P. + density of B at N.T.P.

$$=\frac{\frac{60\times V}{22400}}{5V}+\frac{\frac{40\times 4V}{22400}}{5V}=0{\cdot}001964 \text{ gm./cc.}$$

∵ Total volume of the mixture = 5V.

Gas equation :

45. A soap bubble of 8 cm. diameter containing air at 27°C and 760 mm. pressure is expanded until its radius is 8 cms., the temperature and pressure remaining constant. How many cc.'s of air at S.T.P. are required for the expansion ?

We have, $\dfrac{760\times[\frac{4}{3}\pi(8)^3-\frac{4}{3}\pi(4)^3]}{300}=\dfrac{760\times V}{273}$

or, $V=1709$ cc. $\because\ \pi=\dfrac{22}{7}$.

Miscellaneous :

46. 0·12 gm. of diethyl ether is vaporised in a eudiometer tube of length 100 cms at 98°C. The height of mercury in the tube is lowered to 49 cms. If the barometric pressure is 76 cms. and molecular weight of diethyl ether is 74, calculate the area of cross section of the eudiometer tube.

74 gms of diethyl ether vapour occupy 22400 cc. at N.T.P. $\because$ 1 gm. mole diethyl ether vapour = 74 gms.

$\therefore$ 0·12 gm „ „ occupies $\dfrac{22400\times0{\cdot}12}{74}=36{\cdot}33$ cc. at N.T.P.

Let 'V_1' be the volume of this diethyl ether vapour at 98°C and $(76-49)=27$ cm. pressure.

We have, now $\dfrac{76\times36{\cdot}33}{273}=\dfrac{27\times V_1}{273+98}$ $\therefore\ V_1=139$ cc.

Length of diethyl ether vapour column $=100-49=51$ cms.

$\therefore$ Area of the eudiometer tube $=\frac{139}{51}=2{\cdot}726$ sq. cm.

Ideal gas equation :

47. Two glass bulbs A and B were connected through a stop cock. The bulb A had a volume of 800 ml and it was evacuated,

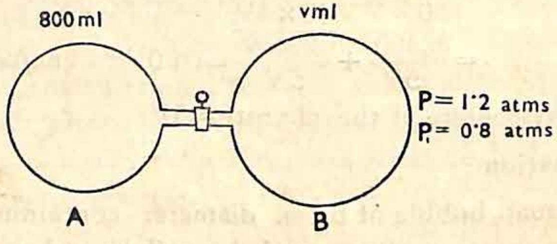


Fig. 15

while the bulb B had an unknown volume and contained a gas at a pressure of 1·2 atmospheres. When the stop cock was opened the pressure of the gas was dropped to 0·8 atmosphere. If the temperature remains constant, what is the volume of the bulb B ?

Temperature is kept constant.

We have, $1{\cdot}2 \times V = {}^{n}\mathrm{B}RT$ ......(i)

$0{\cdot}8(800+V) = {}^{n}\mathrm{B}RT$ ......(ii)

$\therefore\ 0{\cdot}8(800+V) = 1{\cdot}2 \times V$; $V = 1600$ ml.

Miscellaneous :

48. A mixture of hydrogen and water vapour is collected at 20°C in a flask which contains a solid drying agent. Immediately after collection, the pressure in the flask is 760 mm. After sufficient time elapsed, the pressure reaches a steady value of 745 mm. The drying agent increases in weight by 0·150 gm. Calculate the composition of the mixture in mole percent and the volume of the flask.

[Ignore the volume occupied by the drying agent]

Total pressure = P = 760 mm ; partial pressure of water vapour

$= {}^{p}\mathrm{H_2O} = 760 - 745 = 15$ mm ; $\displaystyle {}^{p}\mathrm{H_2O} = \frac{{}^{n}\mathrm{H_2O}\,P}{N}$.

Where, ${}^{n}\mathrm{H_2O}$ = number of moles of water vapour ;

N = total number of moles of the mixture.

$$15 = \frac{{}^{n}\mathrm{H_2O}}{N}\,760 \text{ or } \frac{{}^{n}\mathrm{H_2O}}{N} = \frac{15}{760}.$$

$\therefore$ Mole percent of water vapour $\displaystyle = \frac{{}^{n}\mathrm{H_2O}}{N} \times 100$

$\displaystyle = \frac{15}{760} \times 100 = 1{\cdot}973$; mole per cent of hydrogen

$= 100 - 1{\cdot}973 = 98{\cdot}027$.

We have, $\displaystyle {}^{p}\mathrm{H_2O}\ V = \frac{W}{M}RT$.

Where, $\displaystyle {}^{p}\mathrm{H_2O} = \frac{1{\cdot}5}{76}$ atm ; V = Volume of the flask ;

W = weight of water vapour = 0·15 gm ; M = Molecular weight of water vapour = 18 ; R = universal molar gas constant = 0·0821 ; T = temperature of the water vapour = 273 + 20 = 293°A.

$\therefore \quad \frac{1{\cdot}5}{76} V = \frac{0{\cdot}15}{18} \times 0{\cdot}0821 \times 293$; V = 10·16 litres.

49. A gas mixture containing 80% CO and 20% CO_2 by volume exists at 27°C and 750 mm. pressure. How many grams of CO_2 are present in 1·52 litres of this gas mixture ? [W.B. H.S.C. 1978.]

100 cc mixture contains 80cc CO and 20cc CO_2 at 27°C and 750 mm. pressure.

Again, 100 cc mixture contains 20cc CO_2

Or, 0·1 litre ,, ,, 20cc CO_2

$\therefore$ 1·52 litre ,, ,, $\frac{20 \times 1{\cdot}52}{0{\cdot}1} = 304$cc.

Using the equation $\frac{V_1P_1}{T_1} = \frac{V_0P_0}{T_0}$,

we can write $\frac{304 \times 750}{273+27} = \frac{V_\circ \times 760}{273}$.

$\therefore \quad V_0$ = Volume of CO_2 at N.T.P. $= \frac{304 \times 750 \times 273}{760 \times 300 \times 1000}$ litre.

Amount of CO_2 in gms in 1·52 litres of this gas mixture

$= \frac{44 \times 304 \times 750 \times 273}{22{\cdot}4 \times 760 \times 300 \times 1000} = 0{\cdot}536$. $\because$ 22·4 litre CO_2 at N.T.P. weigh 44 gms.

Avogadro's number and molar concept :

50. What is the number of oxygen atoms in 0·90 gm of water ? [W.B.H.S.C. 1978]

1 gm. mole water contains $6{\cdot}023 \times 10^{23}$ number of molecules of water,

Or, $\frac{0{\cdot}90}{18}$ gm. mole ,, ,, $\frac{6{\cdot}023 \times 10^{23} \times 0{\cdot}90}{18}$ " " ,,

$\because$ Mol. wt. of water = 18.

Again, 1 molecule of water contains 1 atom of oxygen.

$\therefore \quad \frac{6{\cdot}023 \times 10^{23} \times 0{\cdot}90}{18}$ number of molecules of water contains

$\frac{6{\cdot}023 \times 10^{23} \times 0{\cdot}90}{18}$ number of atoms of oxygen

$= 0{\cdot}30115 \times 10^{23}$.

Problems for practice :

1. A dessicator of internal volume one litre and containing nitrogen at one atmosphere pressure is partially evacuated to a final pressure of 7·6 mm. of Hg while the temperature remains constant. What is the volume of the gas at this stage ? [I.I.T. (Group A) 1976]. Ans. 1 litre.

2. A student took readings of the volume of a fixed mass of gas, maintaining the temperature constant while he changed the pressure. His results were

Start	Volume (cc)	Pressure (mm. Hg)
(a)	240	600
(b)	180	800
(c)	144	1000
(d)	108	1200
(e)	90	1600

You can assume that the starting readings are correct and that all the readings are correct but in one of the readings a, b, c, d he made an error in reading the volume : which reading is incorrect ?

3. A cylinder of hydrogen contains 30,000cc of the gas under a pressure of 50 atms. Calculate the number of gas jars each of 400cc. capacity which could be filled up from this cylinder at 750 mm. pressure. Ans. 3800.

4. A balloon containing helium (800 cc) at 75 cm. pressure is allowed to rise to a height of 2000 meters. If the temperature is assumed to be constant, what is the volume of helium at the height of 2000 meters ? [Decrease in atmospheric pressure is about 2·5 cms per 900 ft. rise]. Ans. 1011·0 cc.

5. An air bubble of volume 2·8 cc. is released at the bottom of a water tank of height 25 ft. Calculate the volume of the bubble when it reaches the surface of water. [Atmospheric pressure = 74 cm. Hg] Ans. 4·92 cc.

6. Two balloons are filled with the same gas under the same pressure conditions. One is done at 20°C and the other at 20°A. Predict their extent of bulging. Ans. 14·65.

7. 280 ml. of nitrogen was collected at 300°A. Calculate the temperature at which (a) the volume would be decreased by one half and (b) the volume would be doubled. Pressure is assumed to be constant. Ans. (a) 136·6°A ; (b) 546°A.

8. A rectangular vessel 10 cm. long, 5 cm. wide and 3·5 cm. deep, is filled with hydrogen at 100°C and 77 cm. pressure ; what volume will the gas occupy at N.T.P. ? Ans. 129·8 cc.

9. An open vessel is heated till $\frac{1}{6}$th of hydrogen it contained at 27°C, expelled. To what temperature was the vessel heated ? Ans. 77°C.

10. A specially designed vessel is fitted with a one-way valve. The volume of the vessel is 900 ml. and contains dry hydrogen at 71 cm. pressure and 15°C. To what temperature should the vessel be heated so that 135 ml. of hydrogen escape out under constant pressure ? Ans. 58·2°C

11. A balloon contains 580 cc. helium at 300°K when it is blown to its maximum capacity. If this balloon placed in a refrigerator at 271°K, to what extent will the balloon contract ? Ans. 9·655.

12. 0·3 gm. of a gas occupies 2205 ml. at 70 cm. pressure and 15°C. If at constant temperature, pressure is altered to 220·5 cms, what would be the density of the gas ? Ans. 0·0004285 gm/ml.

13. An open vessel contains air at 27°C. To what temperature should the vessel be cooled so that number of molecules of air in the vessel increases by 40% ? Ignore the contraction of the vessel. Ans. −58·7°C.

14. An open vessel contains air at 27°C. To what temperature should the vessel be heated so that number of molecules in the vessel decreases by 25% ? Ignore the expansion of the vessel. Ans. 127°C.

15. What volume of nitrogen at 16·5°C and 1470 mm. pressure will measure one litre at N.T.P. ?
[*Delhi H. S. 1963*]. Ans. 548·3 ml.

16. A given mass of gas occupies 1520 ml. at 27°C and 700 mm. pressure. What volume will it occupy at S. T. P. ?
[*Sambalpur (Orissa) P. U. 1968*]. Ans. 1274 ml.

17. A cylinder of oxygen contained 120 litres of the gas at 6 atm. pressure. Certain quantity of the gas was taken out from the cylinder, and it is noted that the volume of the gas taken out occupies 15 litres at 1 atm. pressure. Calculate the pressure of the residual oxygen in the cylinder, assuming temperature remaining the same through out the process of removal. Ans. 5·8 atms.

18. When the temperature of 23 ml. of dry carbondioxide gas is changed from 10°C to 30°C at a constant pressure of 760 mm., the volume of gas becomes closest to which one of the following (a) 21·5 ml ; (b) 24·6 ml ; (c) 35 ml.

19. The temperature of the sun is 2×10^7°K. If it is assumed that the gas present on the sun is mainly hydrogen at a pressure of $1{\cdot}2 \times 10^9$ atms, calculate the density of the gas at this temperature and pressure. Ans. 1·462 gm/cc.

20. Two glass cylinders of capacities 600 cc. and 800 cc. are connected through a stop-cock. The cylinder of capacity 600 cc. contains hydrogen at 161 cm. pressure and 15°C. Calculate the change in the pressure when the stop-cock is opened at 115°C. Ignore the expansion of the cylinders. Ans. 68·04 cms.

21. The density of a certain gas is 0·7 gm/lit. at −43°C and 680 mm. pressure. If the density is to be changed to 0·13 gm. per litre at 27°C, how much pressure should be applied?

Ans. 164·7 mm.

22. A balloon of volume 280 cc. at 1 atmospheric pressure is pressed below the surface of ice-cold water (at 5°C temperature) to a depth of 10 meters. Calculate the volume of the balloon, if its initial temperature is 20°C. Ans. 135·04 cc.

23. 40 cc. of oxygen measured at N.T.P. is transferred to a tube of cross section 1·2 sq. cm., sealed at upper end and standing in a trough of mercury, the column of which stands at a height of 15·6 cms. The pressure of the atmosphere is now changed to 75·6 cms and temperature to 304°K. Find the length of the tube containing the gas. Ans. 37·32 cms.

24. 5 gms of ethane are confined in a bulb of one litre capacity. The bulb is so weak that it will burst if the pressure

exceeds 10 atms. At what temperature will the pressure of the of the gas reach the bursting value ? Ans. 458°C.

25. At 380 mm. pressure at 0°C , an 11·2 litre container will hold (a) $\frac{1}{4}$ mole of an ideal gas ; (b) $\frac{1}{2}$ mole of an ideal gas ; (c) 1 mole of an ideal gas ; (d) 2 moles of an ideal gas.

26. The molecular weight of carbon dioxide is 44. Calculate the weight of 600 cc. of this gas at 25°C and 770 mm. pressure.

[*Ranchi. U. P. U. 1971S.*] Ans. 1·09 gm.

27. 6·43 gms of magnesium carbonate on being heated gave 1·27 litres of dry carbon dioxide gas at 27°C and 740 mm. and 4·21 gms. of magnesium oxide. Hence, calculate the molecular weight of carbon dioxide gas. Ans. 44·18.

28. The volume occupied by 1 mole of NH_3 at 0°C and 76 mm. pressure of Hg is (a) 22·4 litres ; (b) 2·24 litres ; (c) 224 litres.

29. Calculate the volume occupied at 20°C and 1 atm of carbon dioxide obtained from **1** cc. of solid carbon dioxide.

(Density = 1·53) Ans. 964·3 cc.

30. The volume of 2·1 gms of a gas at 27°C and 750 mm. pressure is 2400 cc. Calculate the vapour density and molecular weight of the gas. Ans. 10·91 ; 21·82.

31. 10 litres of a gas weigh 28 gms at S.T.P. Calculate the molecular weight of the gas. Ans. 18·26.

32. What weight of oxygen at S.T.P. would occupy a volume of 6·72 litres ? Ans. 9·601 gms.

33. 1 gm of carbondioxide gas was collected in a circular gas jar of height 1 foot at 25°C and 750 mm. pressure. Calculate the radius and diameter of the gas jar. $\left[\text{Hint. } V = 2\pi r.h \text{ ; } PV = \frac{W}{M}RT\right]$

Ans. 2·98 cms ; 5·96 cms.

34. 0·3 gm. mole of a gas is enclosed in a cubical vessel at N.T.P. Find out the length of the cube.

[Hint. $PV = nRT$; $V = L^3$] Ans. 18·9 cms.

35. A gas collected over water occupies 50 cc at 15°C and 740 mm. pressure. The same gas in dry state at N.T.P. occupies 45·3 cc. What is the aqueous tension at 15°C ? Ans. 13·7 mm.

36. A certain gas at 27°C and 746·7 mm. pressure occupied 19 ml. If the same gas occupies 16·4 ml. of volume at S.T.P. Calculate the aqueous tension at 27°C. Ans. 26·7 mm.

37. 0·1 gm of a gas (molecular weight = 60) when collected over water occupied 43·1 cc at 27°C. If the barometric pressure at this temperature is 750 mm, what is the aqueous tension ?

Ans. 26·65 mm.

38. A vessel of capacity 1 litre contains air at 20°C. When the vessel is connected to the vacuum pump the pressure is dropped from atmospheric pressure of 710 mm to 10^{-3} mm at constant temperature. Calculate the molecules of air left in the vessel. Ans. $3{\cdot}257 \times 10^{16}$.

39. 0·068 gm of zinc gave 27 cc of moist hydrogen at 20°C and 750 mm. pressure from dilute sulphuric acid. Calculate the weight of zinc that will liberate 1000 cc of dry hydrogen at S.T.P. (Aqueous tension at 20°C = 17·54 mm.) Ans. 2·8 gms.

40. The two flasks maintained at the same temperature are filled with oxygen gas and sulphur dioxide gas respectively, (i) If the capacities of the two flasks and masses of the two gases are the same, in which flask is the pressure greater and how many times ? (ii) If the pressure and number of molecules in the two flasks are equal, what is the ratio of their volumes ? (ii) Will the number of molecules present in the two flasks be the same or different if the volume of the flasks and pressure of the gases in them are equal ?

41. 100 cc of oxygen are collected over water at 27°C and 800 mm. pressure. Calculate the volume of dry oxygen at N.T.P. (vapour pressure of water at 27°C is 21 mm).

[*Delhi H. S. 1965.*] Ans. 99·54 cc.

42. Prove that : "One gm. nitrogen and one gm. carbon monoxide will contain very nearly the same number of molecules." [N = 14] [W. B. H. S. C. 1979]

43. Choose the correct answer in each of the following. Please note that for each wrong answer one mark will be deducted : (i) A gaseous mixture contains oxygen and nitrogen

in the ratio of 1 : 4 by weight. Therefore, the ratio of their number of molecules is (*a*) 1 : 4 (*b*) 1 : 8 (*c*) 7 : 32 (*d*) 3 : 16. Ans. (*c*). (ii) The largest number of molecules is in (*a*) 36 g of water (b) 28g of carbon monoxide (c) 46g of ethyl alcohol (d) 54g of nitrogen pentoxide. Ans. $2\times 6.023\times 10^{23}$. [*I.I.T. 1979*]

44. 3·7 g of a gas at 25°C occupied the same volume as 0·184g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas ? Ans. 41·32. [*I. I. T. 1979*]

45. The vapour density (hydrogen=1) of a mixture consisting of NO_2 and N_2O_4 is 38·3 at 26·7°C. Calculate the number of moles of NO_2 in 100g of the mixture. Ans. 0·438. [*I. I. T. 1979*]

46. Calculate—(i) gm atoms or moles of oxygen in one mole of nitric acid molecules, (ii) amount of phosphorous and hydrogen present in grams, in 0·2 mole of phosphine, (iii) number of phosphorous and hydrogen atoms in 0·25 mole of phosphine and (iv) the weight, in grams, of one silver atom. [At. wt. P=31, Ag=108] Ans. (i) 3gm atoms or 1·5 gm moles, (ii) 6·2g P and 0·6gH, (iii) $1{\cdot}5\times 10^{23}$ atoms of P and $4{\cdot}51\times 10^{23}$ atoms of H and (iv) $1{\cdot}79\times 10^{-22}$ gms. [W.B.J.E.E. (Tc) 1979]

47. A cylinder contains 0·3 litre oxygen at 12 atm and 0°C, 1 litre of the gas is taken out from the cylinder at N.T.P. Find out pressure of the residual gas in the cylinder.

[**Hints :** $12\times 0{\cdot}3=1\times V_1 \quad \therefore \quad V_1=3{\cdot}6$ litre=vol of O_2 at N. T. P.

Now, 22·4 litre 0_2 at N.T.P. weigh 1gm mole ;

$$3{\cdot}6 \;\text{,,}\;\;\text{,,}\;\;\text{,,}\;\;\text{,,}\;\;\text{,,}\; \frac{1}{22.4}\times 3{\cdot}6 \;\text{,,}$$

Then, $12\times V=\frac{3{\cdot}6}{22{\cdot}4}\times 0{\cdot}0821\times 273.$

Where, V=volume of the vessel.

$$V=\frac{3{\cdot}6\times 0{\cdot}0821\times 273}{22{\cdot}4\times 12}\text{ lit.} \quad \therefore \quad \frac{3{\cdot}6\times 0{\cdot}0821\times 273\times P}{22{\cdot}4\times 12}$$

$$=\frac{2{\cdot}6\times 0{\cdot}0821\times 273}{22{\cdot}4} \quad \therefore \quad P=8{\cdot}66 \text{ atm.}$$

Number of moles of residual oxygen$=\frac{2{\cdot}6}{22{\cdot}4}$]

48. A certain mass of a gas occupies 38 cc at 27°C and 750 mm. pressure. What volume will it occupy at 17°C and 760 mm. pressure ? Ans. 36·25 cc. [*Hyderabad 1977*]

49. A quantity of H_2 collected over water measures 40 cc at 28°C and 765mm pressure. Calculate the weight of the gas if the density of dry H_2 at N.T.P. is 0·09 gm. per litre. Ans. 0·003165 gm. [*Hyderabad. 1976*]

50. Two gases A and B having molecular weight 60 and 45 respectively are enclosed in a vessel. The weight of A is 0·50 gm and that of B is 0·2 gm. The total pressure of the mixture is 750 mm. Calculate the partial pressure of the two gases. Ans. 490·16 mm ; 259·84 mm. [*Roorke Adn. Test. 1973*]

51. 400cc of a gas was collected over water at 17°C and 750 mm. pressure. What will be the volume of the dry gas under standard conditions ? Tension of aqueous vapours at 17°C is 14·4 mm. [*Osmania P.U. 1968*] Ans. 364·6 cc.

52. The atmospheric pressure at a place is 760 mm. of mercury. The air at that place contains water vapour, which alone exerts a pressure of 10 mm. If the dry air is composed of 20% oxygen, 70% nitrogen and 10% carbon dioxide, calculate the partial pressure of each gas. Ans. 150 mm ; 525 mm ; 75 mm.

53. 100 cc. of nitrogen and 50 cc of chlorine both measured at 15°C and 770 mm. pressure are passed into an evacuated flask of 250 cc. capacity. What is the total pressure of the mixture at 20°C ? Ans 47 cms.

54. One gram of hydrogen and 1 gm. of oxygen are put in a 2 litre flask at 27°C. Calculate the partial pressure of each gas, the total pressure, and the composition of the mixture in mole percent. Ans. 0·38 atm ; 6·15 atm ; 6·53 atm ; 5·8% ; 94·2%.

55. A vessel of capacity 1 litre contains 16 gms. of oxygen and 3 gm. liquid water at 27°C. What will be the pressure of the mixture if the water in the vessel is completely vaporised at constant temperature ? Ans. 16·4 atms.

56. A mixture of three gases *X*, *Y* and *Z* is enclosed in a flask at 100 cms at 15°C. The mixture contains 25% *X* and 20% *Z*

by volume. Calculate the pressure of each gas. Ans. 250 mm ; 450 mm ; 300 mm.

57. Air contains 78·06% nitrogen, 21·00% oxygen and 0·94% argon by volume. Calculate the partial pressures of the three gases, if air is at a pressure of 758 mm. Ans. 591·6 mm ; 159·2 mm ; 7·2 mm.

58. If a gm. mole of any gas occupies 22·4 litres at N.T.P., find the volume which 7 gm. of nitrogen would occupy at 27°C and 750 mm. pressure. Ans. 5·95 lits.

59. The volume occupied by 8 gms of O_2 at 546°K and 380 mm. of Hg is...litres, (a) 2·8 ; (b) 44·8 ; (c) 22·4 ; (d) 2·24 ; (e) 4·48.

60. Given that one mole of N_2 at N.T.P. occupies 22·4 litres, the density of N_2 is (a) 1·25 ; (b) 0·80 ; (c) 2·50 ; (d) 1·60 ; (e) 1·50.

61. A mixture of 2 moles of H_2 and 1 mole of He occupies··· litres at N.T.P. (a) 22·4 ; (b) 44·8 ; (c) 67·2 ; (d) 22400 ; (e) data insufficient.

62. A vessel contains a mono-atomic gas whose molecular weight is 80. Calculate the diameter of one single atom of the gas at S.T.P.

[**Hint :** For mono-atomic gas, atomic wt=molecular wt., 1 gm. atom=$6{\cdot}023 \times 10^{23}$ atoms.]

63. 3·93 litres of a certain gas at 25°C and 770 mm. pressure weigh 4·3 gms. What is the weight of 1000 cc of this gas at S.T.P. ? Ans. 1·179 gms.

64. The mass of a molecule of oxygen is (a) $5{\cdot}3 \times 10^{-23}$; (b) 192×10^{-23} ; (c) $5{\cdot}3 \times 10^{23}$; (d) $0{\cdot}2 \times 10^{-23}$.

65. The molecular weight of a gas is 44. What is its density in gm per litre at N.T.P. ? Ans. 1·964.

66. A cylinder of 1 litre capacity is to be filled with hydrogen at 82 atm. pressure at 27°C. What will be the density of hydrogen in the cylinder ? What will be the volume of this hydrogen at N.T.P. ? [*I.I.T (Gp. A) '64*] Ans. 6·667 gms/litre ; 74·62 litres.

67. An automobile tyre registered a pressure of 54 lbs. at a

temperature of 23°C. After driving on a hot pavement, the tyre registered a pressure of 57 lbs ; what was the temperature of the tyre, assuming its volume to remain constant ?

[*Jammu and Kashmir P.U. 1967*] Ans. 39·44°C.

68. A flask can bear pressure upto 1·6 atms. It is filled with oxygen at 283°A and 76·4 cms. It is now heated till the flask explodes. At what temperature does the explosion take place ? Ans. 177·2°*C*.

69. A quantity of a gas is taken in a flask at 25°*C*. To what temperature must the flask be heated to increase the pressure in the flask by 25% ? Ans. 99·5°*C*.

70. Compare the density of air at 10°*C* and 750 mm. pressure with its density at 15°*C* and 760 mm. pressure. Ans. 5400 : 5377.

71. Calculate the density of acetylene at 10°*C* and 3 atms. Ans. 2·067.

72. If the density of a gas is 3·17 gms/litre at N.T.P., what is its molecular weight ? Ans. 71.

73. 0·0263 gm. of magnesium liberates 28 cc. of moist hydrogen at 27°*C* and 757 mm. pressure from dilute acid. Calculate the volume of dry hydrogen that will be liberated at N.T.P. by the action of 1 gm. of magnesium on the dilute acid. (Aq. Tension at 27°*C* = 26·74 mm.) Ans. 931·18 cc.

74. Find the weight of one litre of hydrogen measured at 37°*C* and 800 mm. pressure. [*Orissa, P.U. 1968*] Ans. 0·0834 gm.

[**Hint.** Weight of one litre H_2 at N.T.P. = 0·09 gm.]

75. A balloon has a volume of 500 cc. at 15°*C*, when it is distended to $\frac{4}{5}$ of its maximum stretching capacity. Will it burst if brought into room temperature 27°*C* ? Ans. It will not burst.

76. The molecular weight of a certain gas is 25·55. Calculate the temperature of the gas, if 1·58 gm. of it occupies 1700 cc. at 68 cm. pressure. Ans. 27°C.

77. If the density of water is 1 gm. per. cc. and the volume, occupied by hydrogen molecule and oxygen atom are equal in H_2O, calculate the radius of oxygen atom if volume of water molecule is 3×10^{-23} cc. Ans. $1·53 \times 10^{-8}$ cm.

78. The molecular weights of nitrogen and carbon dioxide are 28 and 44 respectively. If their molecular volume is 22400 cc. at S,T.P., at what temperature carbon dioxide will have the same density as nitrogen at constant pressure ? Ans. 156°C.

79. A certain vessel contains 3·2 gms of argon at S. T. P. What would be the mass of argon contained in the vessel at 200°C and 16 atm. pressure ? *A*ns. 29·54 gms.

80. (a) calculate the number of molecules in a drop of water weighing 0·04 gm. (b) what is volume at N. T. P. of 0·25 gm. atom of chlorine gas ? [*West Bengal H.S.* 1973] Ans. $13{\cdot}39 \times 10^{20}$; 4·55 litres.

81. Calculate the weight of 20 litres of carbon dioxide measured at 0°C and 722 mm. pressure. [*West Bengal H. S.* 1974] Ans. 3·73 gms.

82. Under 740 mm. pressure and at 25°C temperature, 0·15 gm. of a gas occupies a volume of 45·95 cc. Calculate the density and vapour density of the gas at N. T. P. and the molecular weight of the gas. (Density of hydrogen = 0·000089 gm/cc at N. T. P.) [*Calcutta University B. Sc.* 1976. Ans. 41 cc ; 0·0036 gm. cc^{-1} ; 40·4 ; 80·8.

$$\left[\text{Hint. Density} = \frac{\text{wt. of some volume of gas at N.T.P.}}{\text{wt. of same volume of } H_2 \text{ at N.T.P.}};\right.$$

$$\left.\text{Vapour density} = \frac{\text{Molecular wt.}}{2}\right]$$

83. 243 cc of a dry gas at 27°*C* and under a pressure of 770 mm. of Hg weigh 0·28 gm. Calculate the molecular weight of the gas. [*W.B.E.E.* 1970] Ans. 28·011.

84. 250 cc of a gas at N.T.P. weigh 0·7317 gm. The density of hydrogen at N.T.P. is 0·08987 gm/litre. What is the vapour density and density of the gas ? Calculate its molecular weight. [*W.B.E.E.* 1978] Ans. 32·799 ; 32·567 and 65·599.

85. How many molecules of oxygen are there in 1 cc of the gas at N.T.P. ? [*W.B.E.E.* 1976] Ans. $26{\cdot}8 \times 10^{18}$.

86. How many molecules of water are present in a drop of water weighing 0·05 gram ? [*W.B.H.S.C.* (vocational) *1978*] Ans. $1{\cdot}673 \times 10^{23}$.

87. From 200 mg. of CO_2 ; 10^{21} molecules are removed. How many moles of CO_2 are left ? [*I.I.T.* (Gp. A.) *1978*] Ans. 0·002884.

88. What will be the volume in cc of 8·00 gms of oxygen at N.T.P. ? [*W.B.H.S.C.* (vocational) 1978] Ans. 5599 cc.

89. 0·23g of a volatile liquid occupied 126·4 cc at 27°C and 740 mm. pressure. Calculate the molecular weight of the liquid. How many molecules of the liquid are present in 0·23g ?
[*I.S.C.E*1979 Ans. 3×10^{23}.]

CHAPTER 2

Problems on effusion and diffusion of gases

Theory : Phenomenon of issuing a gas from very fine hole made in the wall of a container is known as *effusion.*

Graham's law of effusion : "At constant temperature and pressure, the rates (speeds) of effusion of different gases vary inversely as the square root of their densities." [rate ∝ speed]

If a gas passes out through a porous wall, phenomenon is called *diffusion.*

The aforestated law would also be applicable in the case of diffusion. If R_1 and R_2 be the rates (speeds) of effusion (diffusion) of two gases, having densities d_1 and d_2, at constant temperature (T) and pressure (P), then

$R_1=\dfrac{k}{\sqrt{d_1}}$ and $R_2=\dfrac{k}{\sqrt{d_2}}$, where k is the proportionality constant whose value is constant for the same values of pressure and temperature of gases.

$$\left[\text{Rate of diffusion (effusion)}=\frac{\text{Volume of a gas diffused}}{\text{Time required for this diffusion}}\right]$$

$$\text{Or,}\quad \frac{R_1}{R_2}=\sqrt{\frac{d_2}{d_1}}.$$

Let t_1 and t_2 be the time required for passing out of the same volume (V) of the two gases through the same fine hole.

$$\text{Now,}\ \frac{V}{t_1}=R_1 \text{ and } \frac{V}{t_2}=R_2 \quad \therefore\ \frac{R_1}{R_2}=\frac{t_2}{t_1}=\sqrt{\frac{d_2}{d_1}}$$

Since temperature and pressure are kept constant, the molar volume (V_m) of both the gases must have the same value.

Thus, $\frac{t_2}{t_1}=\sqrt{\frac{d_2 V_m}{d_1 V_m}}=\sqrt{\frac{M_2}{M_1}}$; $\left[\because \; V_m=\frac{\text{Molecular weight}}{\text{Density}}\right]$

where, M_1 and M_2 are the respective molecular weights ;

$\frac{R_1}{R_2}=\sqrt{\frac{M_2}{M_1}}$. Let V_1 and V_2 be the volumes of different gases diffused (effused) in the same interval of time (t).

$$\text{Then, } \frac{R_1}{R_2}=\frac{\frac{V_1}{t}}{\frac{V_2}{t}}=\sqrt{\frac{d_2}{d_1}} \quad \text{or, } \frac{V_1}{V_2}=\sqrt{\frac{d_2}{d_1}} \quad \text{or, } \frac{V_1}{V_2}=\sqrt{\frac{M_2}{M_1}}.$$

Solved problems :

1. The speeds of diffusion of carbon dioxide and ozone were found to be as 0·29 is to 0·274. The relative density of carbon dioxide is 22 when $H=1$. What is the relative density of ozone ? [*Delhi H. S. 1964.*]

We have, $\frac{R_1}{R_2}=\sqrt{\frac{d_2}{d_1}}$ or, $\frac{0·29}{0·274}=\sqrt{\frac{d_2}{22}}$ $\therefore$ $d_2=24·63$.

$\therefore$ the relative density of ozone$=24·63$.

2. 24 ml. of hydrogen diffuse in 180 seconds through a porous disc. 24 ml. of another unknown gas diffuse through the same disc in 195 seconds. Find out the vapour density of the unknown gas. [*All India H. S. 1969*]

We have, $\frac{t_2}{t_1}=\sqrt{\frac{d_2}{d_1}}$ or, $\frac{195}{180}=\sqrt{\frac{d_2}{1}}$ $\therefore d_2=1·173$. $\therefore$ the vapour density of the unknown gas$=1·173$ [Vapour density of hydrogen$=\frac{\text{Mol. wt}}{2}=\frac{2}{2}=1$]

3. If one litre of oxygen diffuses through a small crack in the apparatus in one hour, how long will it take for a litre of chlorine to diffuse through under the same conditions ?

We have, $\frac{t_2}{t_1}=\sqrt{\frac{M_2}{M_1}}$ or, $\frac{t_1}{t_2}=\sqrt{\frac{M_1}{M_2}}$ or, $\frac{1}{t_2}=\sqrt{\frac{32}{71}}$

$\therefore$ $t_2=1{\cdot}48$ hr.

4. The speeds of diffusion of carbon dioxide and ozone were found to be 0·58 and 0·542. If the molecular weight of carbon dioxide be 44, what is the molecular weight of ozone ?

[*Calcutta University, B. Sc. 1969, '70*]

$$\frac{R_1}{R_2}=\sqrt{\frac{M_2}{M_1}};\quad \frac{R_{CO_2}}{R_{O_3}}=\sqrt{\frac{M_{O_3}}{M_{CO_2}}}\quad \text{or,}\quad \frac{0{\cdot}58}{0{\cdot}542}=\sqrt{\frac{M_{O_3}}{44}}$$

$\therefore$ $M_{O_3}=50{\cdot}39$.

5. 30 ml. of ozone diffuse in the same time as 25 ml. of chlorine. If the density of chlorine is 35·4, calculate the density of ozone. [*Aligarh P. U. 1967.*]

We have, $\frac{V_1}{V_2}=\sqrt{\frac{d_2}{d_1}}$ or, $\frac{30}{25}=\sqrt{\frac{35{\cdot}4}{d_1}}$ $\therefore$ $d_1=24{\cdot}6$.

6. 100 cc. of sulphur dioxide diffuse in 31·1 seconds. What volume of nitrogen would diffuse in the same time ?

We have, $\frac{V_1}{V_2}=\sqrt{\frac{M_2}{M_1}}$ or. $\frac{100}{V_2}=\sqrt{\frac{28}{64}}$ $\therefore$ $V_2=151{\cdot}18$ cc.

7. Calculate the molecular weight of an unknown gas which under precisely similar condition takes 1·117 times as long as oxygen to diffuse through an aperture. [*Ranchi.* U. 1971]

We have, $\frac{t_1}{t_2}=\sqrt{\frac{M_1}{M_2}}$ or, $1{\cdot}117=\sqrt{\frac{M_1}{32}}$ $\therefore$ $M_1=39{\cdot}93$.

$\therefore$ molecular weight of an unknown gas $=39{\cdot}93$.

8. How long will it take 750 ml. of chlorine to diffuse through a porous partition if 300 ml. of oxygen diffuse through the same partition in 50 seconds ? [*Rajasthan P.U. 1966*]

We have, $\frac{R_1}{R_2}=\frac{\frac{V_1}{t_1}}{\frac{V_2}{t_2}}=\sqrt{\frac{M_2}{M_1}}$ or, $\frac{V_1t_2}{V_2t_1}=\sqrt{\frac{M_2}{M_1}}$.

Here, $V_1 = 750$ ml. ; $V_2 = 300$ ml. ; $t_1 = ?$ $t_2 = 50$ seconds ; $M_1 = 35{\cdot}5 \times 2 = 71{\cdot}0$; $M_2 = 32$.

$$\text{or, } \frac{750 \times 50}{300 \times t_1} = \sqrt{\frac{32}{71}} \qquad \therefore \; t_1 = 186{\cdot}2 \text{ seconds.}$$

9. Ladenburg found that ozonised oxygen containing 86·16% of ozone by volume required 430 seconds to diffuse, where as the same volume of oxygen required 367·4 seconds under the same conditions. Find the density of ozone.

V is assumed to be the volume diffused out in each case. Let D, do_2 and do_3 be the densities of the mixrure, pure oxygen and ozone respectively.

$$\frac{R_1}{R_2} = \frac{\frac{V}{430}}{\frac{V}{367{\cdot}4}} = \sqrt{\frac{do_2}{D}} = \sqrt{\frac{16}{D}}.$$

[$\because$ vapour density $= \frac{\text{mol. wt.}}{2}$; $do_2 = \frac{32}{2} = 16$]

$$\text{or, } \frac{(367{\cdot}4)^2}{(430)^2} = \frac{16}{D} \qquad \text{or, } D = \frac{16 \times (430)^2}{(367{\cdot}4)^2} = 21{\cdot}92.$$

We know that,

mass of mixture = mass of pure oxygen + mass of pure ozone.

For 100 cc. volume of the mixture,

$$21{\cdot}92 \times 100 = do_3 \times 86{\cdot}16 + 16 \times (100 - 86{\cdot}16)$$

$\because$ Density $= \frac{\text{Mass}}{\text{Volume}}$; Mass = Density × Volume.

$$\text{or, } 2192 = do_3 \times 86{\cdot}16 + 16 \times 13{\cdot}84$$

$$\text{or, } do_3 \times 86{\cdot}16 = 2192 - 13{\cdot}84 \times 16$$

$$\text{or, } do_3 = \frac{2192 - 221{\cdot}5}{86{\cdot}16} = \frac{1970{\cdot}5}{86{\cdot}16} = 22{\cdot}88.$$

10. 10 litres of hydrogen are placed in a porous partition cylinder with an equal volume of nitrogen. If the speed of

diffusion of hydrogen from this cylinder is 0·5 litre/hr., what will be the proportion of gases in the cylinder after 90 minutes ?

We have,

$$\frac{\frac{V_{H_2}}{t_{H_2}}}{\frac{V_{N_2}}{t_{N_2}}}=\sqrt{\frac{D_{N_2}}{D_{H_2}}} \quad \text{or} \quad \frac{V_{H_2}\times t_{N_2}}{V_{N_2}\times t_{H_2}}=\sqrt{\frac{D_{N_2}}{D_{H_2}}}.$$

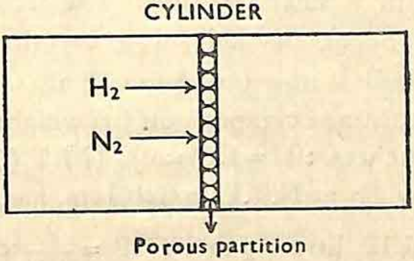


Fig. 16

Here, V_{H_2} = volume of hydrogen diffused = 0·5 ;

V_{N_2} = volume of nitrogen diffused ;

t_{H_2} = time required for diffusion of hydrogen = 1 hr ;

t_{N_2} = time required for diffusion of nitrogen = 1 hr ;

D_{H_2} = density of hydrogen = 1 ;

D_{N_2} = density of nitrogen = 14.

$$\frac{0\cdot5\times1}{V_{N_2}\times1}=\sqrt{\frac{14}{1}} \quad \therefore \quad V_{N_2}=0\cdot1337 \text{ litre.}$$

Volume of hydrogen diffused after 90 minutes = 0·5 × 1·5 = 0·7501 litre ; volume of nitrogen diffused after 90 minutes = 0·1337 × 1·5 = 0·2005 litre.

Volume of hydrogen remains undiffused in the L. H. S. of the cylinder (Fig. 16) after 90 mints.

= 10 − 0·7501 = 9·2499 ≈ 9·25 litres.

Volume of nitrogen remains undiffused in the L. H. S. of the cylinder (Fig. 16) after 90 mints. $=10-0{\cdot}2005=9{\cdot}7995\approxeq 9{\cdot}80$ litres.

$\therefore$ the proportion of hydrogen and nitrogen in the left hand side of the cylinder after 90 minute inteval of time $=\frac{9{\cdot}25}{9{\cdot}80}=\frac{185}{196}$.

11. A mixture containing 1·12 litres of H_2 and 1·12 litres of D_2 at N.T.P. is taken inside a bulb connected to another bulb by a stopcock with a small opening. The second bulb is fully evacuated, the stopcock opened for a certain time, and then closed. The first bulb is now found to contain 0·05 gm. of H_2. Determine the percentage composition by weight of the gases in the second bulb. [At wts. : H=1, D=2] [*I.I.T (Group A)* 1976.]

22·4 litres of any gas at N.T.P. weigh 1gm. mole.

$\therefore$ weight of 1·12 litre H_2 at N.T.P. $=\frac{2}{22{\cdot}4}\times 1{\cdot}12=0{\cdot}1$ gm.

Weight of 1·12 litre D_2 at N.T.P. $=\frac{4}{22{\cdot}4}\times 1{\cdot}12=0{\cdot}2$ gm.

$\because$ 1 gm. mole = molecular weight expressed in gms.

Now, the volume of 0·05 gm. H_2 at N.T.P. $=\frac{22{\cdot}4}{2}\times 0{\cdot}05$

$=0{\cdot}56$ lits. This 0·56 litre H_2 remains uneffused after *t* sec.

$\therefore$ the volume of H_2 effused out of the 1st bulb after *t* sec.

$=1{\cdot}12-0.56=0{\cdot}56$ lits.

Let the volume of D_2 effused out of the 1st bulb in the same time (*t* sec) be V_{D_2} expressed in litres.

Then, rate of effusion of $H_2=\frac{0{\cdot}56}{t}$; rate of effusion of $D_2=\frac{V_{D_2}}{t}$. We have now, $\frac{R_{H_2}}{R_{D_2}}=\sqrt{\frac{M_{D_2}}{M_{H_2}}}$.

$$\text{or,}\quad \frac{0{\cdot}56/t}{V_{D_2}/t}=\sqrt{\frac{4}{2}}\quad \therefore\quad V_{D_2}=0{\cdot}4\ \text{litre.}$$

∴ the volume of D_2 effused at N.T.P. into the 2nd bulb $= 0{\cdot}4$ litre ; the weight of 0·4 litre D_2 at N.T.P.

$$= 0{\cdot}4 \times \frac{4}{22{\cdot}4} = 0{\cdot}07 \text{ gm.}$$

The weight of hydrogen in the 2nd bulb $= 0{\cdot}1 - 0{\cdot}05 = 0{\cdot}05$ gm. Thus, the 2nd bulb contains 0·07 gm. of D_2 and 0·05 gm. of H_2

$$\therefore \ \% \text{ of } D_2 = \frac{0{\cdot}07}{0{\cdot}12} \times 100 = 58{\cdot}3 \ ;$$

$$\% \text{ of } H_2 = \frac{0{\cdot}05}{0{\cdot}12} \times 100 = 41{\cdot}7 \quad \therefore \text{ total wt. of } (H_2 + D_2)$$

mixture in the 2nd bulb $= 0{\cdot}05 + 0{\cdot}07 = 0{\cdot}12$ gm.

12. 100 cc. hydrogen are confined in one side of a cylinder partitioned with a porous wall. A sample of air is in the other side of the cylinder. Diffusion takes place. After sufficient time find the composition of gases in the two compartments, given the densities of hydrogen and air respectively as 0·09 and 1·293 gm. per litre.

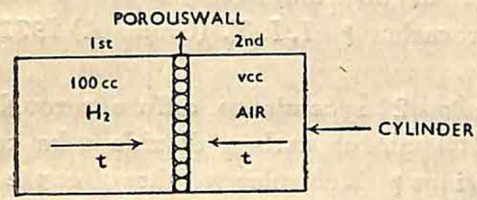


Fig. 17

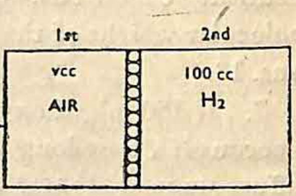


Fig. 18

$$\text{We have, } \frac{\frac{V}{t}}{\frac{100}{t}} = \sqrt{\frac{0{\cdot}09}{1{\cdot}293}} \ ;$$

$V = 26{\cdot}4$ cc. ∴ at the end of diffusion, 100 cc. hydrogen have come to the 2nd compartment, at the same time interval $V = 26{\cdot}4$ cc of air, entered 1*st* compartment.

Problems for practice :

1. 57 ml. of hydrogen takes the same time for diffusion through a porous vessel as 10 ml. of another gas G. Calculate the molecular weight of G. *Panjab. P.U.* 1969. Ans. 64·98.

2. A unknown gas diffuses four times as quickly as oxygen. Calculate the molecular weight of the gas. *Panjab. P. U.* 1964. Ans. 2.

3. The relative rate of diffusion of a gas A as compared with chlorine is as 6 : 5. Taking the vapour density of chlorine as 36, calculate the molecular weight of the gas A. *Bihar H.S. 1964.* Ans. 50.

4. Calculate the relative rates of diffusion of $^{235}UF_6$ and $^{233}UF_6$ in the gaseous form. (At. wt. : $F=19$) *I. I. T. (Group B) 1976.* Ans. 1·0043 : 1·0000.

5. 2 ml. ozone takes the same time for diffusion through a porous tube as 9·8 ml. of hydrogen ? Calculate the vapour density and molecular weight of ozone if the vapour density of hydrogen=1. *Kashmir Inter, 1960.* Ans. 24·01 ; 43·02.

6. 180 ml. of a hydrocarbon diffuse through a porous membrane in 15 minutes while 120 ml. of sulphur dioxide, under identical conditions, diffuse in 20 minutes. What is the molecular weight of the hydrocarbon ? *I. I. T. (Group A) 1971.* Ans. 16.

7. If 150 ml. of oxygen takes 25 seconds to diffuse through a porous lid, how long will 200 ml. of carbon dioxide take to diffuse under the same conditions ? Molecular weights of oxygen and carbon dioxide are 33 and 44 respectively. *Bihar H. S. 1962.* Ans. 39·08 seconds.

8. If 100 volumes of air take 9 seconds to diffuse from a vessel, how long would it take the same volume of chlorine to do under similar conditions ? Densities of air and chlorine are being 14·4 and 35·5 respectively. *Panjab P. U. 1967*. Ans. 14·13 seconds.

9. If 50ml. of hydrogen take 10 minutes to diffuse out of a vessel how much time will be required for 75 ml. of chlorine to diffuse under the same conditions ? How fast will hydrogen diffuse as compared to chlorine ? Relative density of hydrogen is 1 and that of chlorine is 36. *Marathwada P. U.* 1969. Ans. 90 mints.

10. Calculate the rate of diffusion of hydrogen gas when 950 cc. of it diffused out in 60 seconds through a porous partition. How many seconds would be required to diffuse 1560 ml. of the gas at this rate ? Ans. 16cc/sec ; 97·5 seconds.

11. Ladenburg found that a sample of ozonised oxygen containing 86·16% of ozone by weight required 430 seconds to diffuse under conditions where pure oxygen required 367·5 seconds. Determine the vapour density of ozone. Ans. 23·3.

12. A given volume of ozonised oxygen containing 20% by volume of ozone, required 175 seconds to diffuse, while an equal volume of oxygen required only 168 seconds under the same conditions. Find the vapour density of ozone. *Magadh U. I. Sc. 1970A ; Madhya Pradesh. Inter science. 1964.* Ans. 22·8.

13. The rate of diffusion of a certain gas A having molecular weight 60 is 5·121 cc per second. What would be the rate oil diffusion of oxygen ? Ans. 7·012 cc/sec.

14. 16 cc. of a gas A were found to diffuse in 30 seconds. What volume of another gas B would diffuse in the same interval of time under the same conditions of pressure and temperature ? Mol. wt. of A=2 ; Mol. wt. of B=64. Ans. 2·828 cc.

15. The relative rate of diffusion of a sample of ozonised oxygen and chlorine was noticed to be as 5·95 : 4·08. Calculate the percentage of ozone in the ozonised oxygen. Mol. wt. of ozone=48 ; Mol. wt. of chlorine=71. Ans. 8·625%.

16. 25 cc. of oxygen diffuse through a porous partition in 100 seconds. What volume of carbon dioxide will diffuse in the same time under the same conditions of temperature and pressure ? Ans. 21·32 sec.

17. Calculate volume of nitric oxide which will diffuse out of a porous wall in 10 seconds, when 25 cc of methane gas diffuse out in 4 seconds. [Relative density of nitric oxide=15 ; Relative density of CH_4=8] Ans. 45·64 cc.

18. Compare the times of diffusion through a given orifice, under the same conditions of temperature and pressure, of the gases : H_2, NH_3 and CO_2, relative to that of N_2, using the

known molecular weights of the gases. *Calcutta University. B. Sc. 1976.* Ans. $\frac{1}{3.75}$; $\frac{1}{1.283}$; $\frac{1}{0.797}$.

19. Choose the appropriate answer :—The rates of diffusion of two gases X and Y are in the ratio 1:3. The molecular weight of Y is 2. The molecular weight of gas X is (i) 9, (ii) 18, (iii) 27, (iv) 36·0. *Sambalpur (Orissa) H. S. 1978.*

20 Deduce the relative rates of diffusion of the following gases hydrogen, ammonia, carbon dioxide. *Patna U. 1970A.* Ans. 4·7 : 1·612 : 1.

21. A non metallic gaseous oxide contains 50% oxygen. The relative speeds of diffusion of carbon dioxide (CO_2) and gaseous oxide were 1·2 : 1. Find the equivalent weight of the non metal. *Magadh U. I.Sc. 1969A.* Ans. 8.

22. 250 cc. of oxygen take 100 seconds to diffuse. What volume of CO_2 gas will diffuse under like conditions in 150 seconds ? *Bihar U. 1961 A ; Ranchi U. I. Sc. 1962 A, 1973 A.* Ans. 319·8 cc.

23. The speeds of diffusion of carbon dioxide and another gas were found to be in the ratio of 0·29 to 0·271. Given that the molecular weight of carbon dioxide is 44, find the molecular weight of the second gas. *Hyderabad I. Sc. 1974.* Ans. 50·39.

24. The densities of hydrogen and oxygen are in the ratio 1 : 16. If 20 cc of hydrogen diffuse out of a porous vessel in 100 seconds, what time will the same volume of oxygen take to diffuse under the same conditions ? *Hyderabad I. Sc. 1976.* Ans. 400 seconds.

25. 100 ml hydrogen take 20 minutes to diffuse in a porous vessel. How long will take to diffuse 40 ml oxygen under like conditions ? *Lalit Narayan Mithila U. 1976A (I.Sc.)* Ans. 32 mints.

26. Show that the rate of diffusion of hydrogen is four times that of oxygen. *Hyderabad. I. Sc. 1977.*

27. Relative rates of diffusion of ozone as compared with chlorine is 6:5. If the density of chlorine is 35·5, find the density of ozone. *Indian School Certificate Examination, 1978.* Ans. 24·652.

28. 1 litre of hydrogen diffuses through a porous pot in 95 secs. What is the molecular weight of an unknown gas, 1 litre of which diffuses through the same pot in 5 minutes 55secs. under the same conditions ? *Ranchi U. 1979.* Ans. 27·93.

CHAPTER 3

Problems on Chemical equilibrium

Chemical equilibrium : is the state of a reversible homogeneous reaction in which the rate of forward reaction is the same as that of the backward reaction.

Law of mass action :—

This law states according to Guldberg and Waage that the rate (speed) of a chemical reaction is proportional to the product of the active masses of the reacting substances at the instant from the commencement of the reaction at constant temperature.

Active mass :—

Active mass is a unit of concentration, can be defined as the number of gm. moles of a substance present per unit volume of the reaction mixture. This mass is active in helping production of further amount of products.

Rate (speed) of a chemical reaction :—

A very small amount of a reactant or each reactant (in equal amount), used for production of product or products per unit time interval is known as rate (speed) of a chemical reaction.

X_1 = amount of reactant (in gm. mole/litre) at the start of the reaction when time recorded is t_1 (sec).

X_2 = amount of reactant unused after Δt (sec) time interval from the very start of the reaction.

$\therefore$ $X_1 - X_2$ = amount of reactant used after Δt interval of time.

or, $X_1 - X_2 = \Delta X$; where ΔX = difference in amount of the reactant.

Again, $\Delta t = t_2 - t_1$; t_2 = time recorded when Δt time elapsed from the commencement of the reaction.

Now, $\frac{\Delta X}{\Delta t} \neq$ rate of the reaction but $\underset{\Delta t \to 0}{\mathrm{Lt}} \frac{\Delta X}{\Delta t}$ = rate of the reaction$=\frac{dX}{dt}$. As rate increases with time, rate is determined, considering a very small time interval on introducing limiting idea. Here, $\frac{dX}{dt}$ represents rate or speed of a chemical reaction.

Let a=initial amount of a reactant in gm. mole/litre ;

X=amount of the reactant used in t sec. time interval ;
$a-X$=amount of the reactant unused after t time.

Then, rate of the reaction$=\frac{-d(a-X)}{dt}$.

$$\text{or, } \frac{-d(a-X)}{dt}=-\frac{da}{dt}+\frac{dX}{dt}=\frac{dX}{dt} \quad \because \ a=\text{constant.}$$

Active mass$=\frac{a-X}{V}$; V=volume of the vessel where reaction takes place.

For the reversible homogeneous reaction

$$A+B \rightleftharpoons C+D$$

$$K_C=\frac{C_C \times C_D}{C_A \times C_B}=\frac{[C]\ [D]}{[A]\ [B]}.$$

$$\because \quad K_C=\frac{\text{Rate constant of forward reaction}}{\text{Rate constant of backward reaction}}.$$

Where '[ ]', the symbol represents concentration at the equilibrium stage and K_c is the equilibrium constant in terms of concentrations at the temperature $T°A$.

For a general homogeneous reversible reaction ;

$$aA+bB \rightleftharpoons gC+hD :$$

$$K_C=\frac{C_C{}^g \times C_D{}^h}{C_A{}^a \times C_B{}^b}=\frac{[C]^g\ [D]^h}{[A]^a\ [B]^b}.$$

If the component gases behave ideally or approximate closely ideal behaviour, concentration of each component of the reaction is proportional to its partial pressure.

$$\therefore \quad K_P=\frac{p_C{}^g \times p_D{}^h}{p_A{}^a \times p_B{}^b} ;$$

Where, K_p = equilibrium constant interms of partial pressures at T°A.p stands for partial pressure.

$K_p = K\ (RT)^{\Delta n}$; where, Δn is a difference in the sum of moles of the reactants from that of the products.

For the **homogeneous gaseous dissociation,**

$AB_b \rightleftharpoons A + bB$, at equilibrium when the fraction α (degree of dissociation) of 1 mole AB_b has dissociated, the number of moles of A produced from AB_b is then α ; the number of moles of B is $b\alpha$; and the number of moles of AB_b intact is $(1-\alpha)$. Total number of moles of gas mixture at equilibrium is $1-\alpha+b\alpha+\alpha = 1+b\alpha$. If the total pressure of the mixture becomes P, then applying Dalton's law of partial pressures (vide. Chapter 1), we can write at equilibrium,

$$p_A = \frac{n_A}{N}P = \frac{\alpha}{1+b\alpha}P; \quad p_B = \frac{n_B}{N}P = \frac{b\alpha}{1+b\alpha}P \text{ and}$$

$$p_{AB_b} = \frac{n_{AB_b}}{N}P = \frac{1-\alpha}{1+b\alpha}P.$$

On substitution these partial pressure values in the expression

$$K_p = \frac{p_A . p_B}{p_{AB_b}}$$

we can write, $$K_p = \frac{\frac{\alpha}{1+b\alpha}P.\left(\frac{b\alpha}{1+b\alpha}P\right)^b}{\frac{1-\alpha}{1+b\alpha}P} = \frac{\alpha(\alpha bP)^b}{(1-\alpha)(1+b\alpha)^b}.$$

When $b=1$; then $K_p = \frac{\alpha^2 P}{1-\alpha^2}$.

Examples : (i) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$;

[(g) represents gaseous state]

(ii) $NH_4Cl_{(g)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$;

(iii) $COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$.

The reaction where the products of dissociation are indistinguishable, can be written as

$$A_{b+1} \rightleftharpoons (b+1)\,A.$$

This equation can never be expressed as

$$A_{b+1} \rightleftharpoons bA + A.$$

Where bA has been distinguished from A which is apparently impossible.

Here, $p_A = \frac{(b+1)\alpha}{1+b\alpha}P$ and $p_{A_{b+1}} = \frac{1-\alpha}{1+b\alpha}P.$

On substitution these partial pressure values in the expression

$$K_p = \frac{p_A^{(b+1)}}{p_{A_{b+1}}}$$

we can write,

$$K_p = \frac{\left\{\frac{(b+1)\alpha}{1+b\alpha}P\right\}^{b+1}}{\frac{1-\alpha}{1+b\alpha}P} = \frac{\{(b+1)\alpha\}^{b+1}P^b}{(1+b\alpha)^b(1-\alpha)}.$$

When $b=1$, as in the case of diatomic molecule A_2, the reaction is $A_2 \rightleftharpoons 2A$, can never be written as,

$$A_2 \rightleftharpoons A + A.$$

Then, $K_p = \frac{4\alpha^2 P}{1-\alpha^2}.$

Examples : (i) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$;

(ii) $I_{2(g)} \rightleftharpoons 2I_{(g)}$.

N. B. Diatomic molecule : one molecule comprises two atoms.

$\alpha = \frac{d_0 - d}{(n-1)d}$; where, one molecule of a substance splits up into n molecules on heating ;

d_0 = true vapour density assuming nil dissociation ;

d = apparent or observed vapour density when dissociation has occurred ; α = degree of dissociation. $d_0 = \frac{M}{2}$, according to

Avogadro. Where, M represents molecular weight of the substance.

For, $NH_4Cl_{(g)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

$n - n\alpha \quad n\alpha \quad n\alpha$

$PV = (n + n\alpha)\,RT$ for $(n + n\alpha)$ gm mole of the above mixture after dissociation. Assuming that the mixture behabes ideally.

P = total pressure, exerted by the mixture of ammonia, hydrogen chloride and undissociated ammoniun chloride ;

V = volume of the vessel where reaction sets in ;

n = total number of moles of ammonium chloride before dissociation , T is the temperature at which dissociation goes on R = universal molar gas constant.

or, $PV = n(1+\alpha)RT$; $PV = \frac{W}{M}(1+\alpha)RT \quad \because \quad n = \frac{W}{M}$.

W stands for weight in gms. of the substance.

For, $I_{2(g)} \rightleftharpoons 2I_{(g)}$

$n - n\alpha \quad 2n\alpha$

$PV = (n - n\alpha + 2n\alpha)RT$ or, $PV = (n + n\alpha)RT$.

Thermal dissociation of hydrogen sulphide

$$2H_2S_{(g)} \rightleftharpoons 2H_{2\,(g)} + S_{2(g)}$$

$$2 - 2\alpha \qquad 2\alpha \qquad \alpha$$

Total number of moles of the mixture at the equilibrium $= 2 - 2\alpha + 2\alpha + \alpha = 2 + \alpha$.

$$p_{H_2S_{(g)}} = \frac{2-2\alpha}{2+\alpha}P \;;\; p_{H_{2\,(g)}} = \frac{2\alpha}{2+\alpha}P \;;$$

$$p_{S_{2(g)}} = \frac{\alpha}{2+\alpha}P.$$

On substitution these values of partial pressure in the expression $K_p = \frac{p^2_{H_2(g)} \cdot p_{S_{2(g)}}}{p^2_{H_2S_{(g)}}}$, we can write $$K_p=\frac{\left(\frac{2\alpha}{2+\alpha}P\right)^2\times\frac{\alpha}{2+\alpha}P}{\left(\frac{2-2\alpha}{2+\alpha}P\right)^2}=\frac{\alpha^3P}{(2+\alpha)(1-\alpha)^2}.$$

Where, P stands for total pressure of the mixture ; α = degree of dissociation.

Synthesis of ammonia

$$N_{2(g)}+3H_{2(g)}\rightleftharpoons 2NH_{3(g)}$$
$$1-X \quad 3-3X \quad 2X$$

Total number of moles of the mixture at the equilibrium

$$=1-X+3-3X+2X=4-2X.$$

Thus, $$K_p=\frac{16X^2(2-X)^2}{27(1-X)^4\,P^2}.$$

Where, P = total pressure ;

X = amount of each reactant used from 1 gm. mole.

Formation of sulphur trioxide

$$2SO_{2(g)}+O_{2(g)}\rightleftharpoons 2SO_{3(g)}$$
$$2-2X \quad 1-X \quad 2X$$

Total number of moles of the mixture at the equilibrium

$$=2-2X+1-X+2X=3-X.$$

Thus, $$K_p=\frac{2X^2(3-X)}{(1-X)^2P}.$$

Synthesis of nitric oxide

$$N_{2(g)}+O_{2(g)}\rightleftharpoons 2NO_{(g)}$$
$$a-X \quad b-X \quad 2X$$

Pressure consideration

If 'a' moles of nitrogen (N_2) and 'b' moles of oxygen (O_2) are taken initially and if $2X$ moles of nitric oxide (NO) are formed at equilibrium, we have, total number of moles of the mixture $=a-X+b-X+2X=a+b$; number of moles of unused nitrogen

$=a-X$; number of moles of unused oxygen $=b-X$ and number of moles of nitric oxide formed $=2X$.

$$\text{Now, } K_p=\frac{p^2_{NO}}{p_{N_2}\cdot p_{O_2}}=\frac{\left(\frac{2X}{a+b}P\right)^2}{\left(\frac{a-X}{a+b}\right)P\cdot\left(\frac{b-X}{a+b}\right)P}$$

$$=\frac{4X^2}{(a-X)(b-X)}.$$

Where, P stands for total pressure.

Volume Consideration

$$K_c=\frac{[NO]^2}{[N_2]\,[O_2]}=\frac{\left(\frac{2X}{V}\right)^2}{\left(\frac{a-X}{V}\right)\left(\frac{b-X}{V}\right)}=\frac{4X^2}{(a-X)(b-X)}.$$

Where, $V=$ Volume of the vessel expressed inlit, active mass of NO $=\frac{2X}{V}$; active mass of $N_2=\frac{a-X}{V}$ and active mass of $O_2=\frac{b-X}{V}$.

Esterification of acetic acid by ethyl alcohol

This reaction is represented by the following equation,

$$CH_3COOH+C_2H_5OH\rightleftharpoons\downarrow CH_3COOC_2H_5+\downarrow H_2O$$

(Liquid acetic acid) (Liquid ethyl alcohol) (Liquid ethyl acetate) (water)

If 'a' moles of acetic acid and 'b' moles of ethyl alcohol are initially taken and if X moles of ethyl acetate are produced at the equilibrium stage, we have,

$$K_c=\frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH]\,[C_2H_5OH]}=\frac{X^2}{(a-X)(b-X)}.$$

Le Chatelier's principle (1885)

The Chatelier's principle

Statement in French as well as in English :

Quant un systéme á équilibre est assujetti á une

When a system at equilibrium is subjected to a

force (comme changement du pression, temperature et concentration)

stress (such as change of pressure, temperature and concentration),
le systéme ira á la direction où il
the system will go to that direction where it
se soulage de la force.
itself relieves of that stress.

Example : (i) The equilibrium mixture of NO_2 (gas) + CO (gas) $\rightleftharpoons$ CO_2 (gas) + NO (gas) exists at a definite temperature and at a total pressure of 2 atm. If the total pressure be increased to 4 atm will the amount of products increase, decrease or remain the same ? Explain your answer.

(ii) In the above reaction, if the partial pressure of CO be increased by introducing more CO into the system from outside, how will the amount of products be affected ? (Answer only in qualitative terms) W.*B.H.S.C.* 1978.

(i) The number of moles is the same on both sides of the equation and there is no change in volume. Therefore a change of pressure (2 atm to 4 atm) at definite temperature and concentration has no effect on the reaction. Hence, the amount of products remains the same with the increase of total pressure to 4 atm.

(ii) At definite temperature and pressure, on the introduction of more CO into the system from outside, the amount of products will increase. According to le Chatelier's principle the reaction will go to that direction where it can diminish some of additional number of moles of CO. Thus, forward reaction is favourable with the formation of more products. Diminution is possible only when there is further reaction in the forward direction.

System : A homogeneous reversible reaction or a heterogeneous reversible reaction.

Heterogeneous reaction : In this type of reaction components are neither in same phase nor in definite proportion.

Homogeneous reaction : In this type of reaction components are in same phase and in definite proportion.

System at equilibrium : System is at definite temperature, pressure and concentration of each component of the reaction mixture.

Subjected to a stress : Variation of temperature, pressure and concentration. Temperature is varied keeping pressure and concentration constant, pressure is altered keeping temperature and concentration constant and concentration is changed at definite temperature and pressure.

Solved Problems :

1. For an equilibrium reaction, the rate constant for the forward reaction and the backward reaction is $2{\cdot}38\times10^{-4}$ and $8{\cdot}15\times10^{-5}$ respectively. Find out the equilibrium constant for this reaction.

We have, equilibrium constant

$$=\frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}}$$

$$\text{Or, } K_c=\frac{2{\cdot}38\times10^{-4}}{8{\cdot}15\times10^{-5}}=2{\cdot}92.$$

2. One mole of A and one mole of B are mixed in a volume of one litre. If 0·9 mole per litre of C is found at following equilibrium reaction,

$$A_{(g)}+B_{(g)}\rightleftharpoons C_{(g)}+H_{(g)},$$

find out the equilibrium constant interms of concentrations.

$$\text{We have, } K_c=\frac{\frac{0{\cdot}9}{1}\times\frac{0{\cdot}9}{1}}{\frac{1-0{\cdot}9}{1}\times\frac{1-0{\cdot}9}{1}}=81.$$

$$\because\quad \begin{array}{cccc} A_{(g)}+ & B_{(g)}\rightleftharpoons & C_{(g)}+ & H_{(g)} \\ \frac{1-X}{V} & \frac{1-X}{V} & \frac{X}{V} & \frac{X}{V} \end{array}$$

Here, $X=0{\cdot}9$; $V=1$ litre.

3. Under equilibrium conditions the amount of HI in a 3 litre vessel was 12·8 gms. Find out the equilibrium concentration of HI.

$$\text{Equilibrium concentration of } HI=\frac{\frac{12{\cdot}8}{M}}{3}.$$

Where, M = molecular weight of $HI=1+127=128.$

$$\text{or,} \quad =\frac{\frac{12{\cdot}8}{128}}{3}=\frac{12{\cdot}8}{128\times 3}=0{\cdot}033 \text{ mole/lit.}$$

4. When alcohol and acetic acid are mixed together in equimolecular proportions 66·5% are converted into ester. Calculate how much ester would be produced if one mole of acetic acid is treated respectively with 0·5,4 and 8 moles of alcohol.

Gorakhpur U. 1961 ; Patna U. 1967.

Equation of the reacrion is,

$$\underset{a-X}{C_2H_5OH}+\underset{b-X}{CH_3COOH}\rightleftharpoons\underset{X}{CH_3COOC_2H_5}+\underset{X}{H_2O}$$

Where, a = initial number of moles of C_2H_5OH per litre ;

b = „ „ „ „ „ CH_3COOH „ „ ;

X = number of moles of C_2H_5OH and CH_3COOH per lire used = number of moles of $CH_3COOC_2H_5$ and H_2O per litre formed ;

$a-X$ = number of moles of C_2H_5OH per litre unused and

$b-X$ = number of moles of CH_3COOH per litre unused.

$$\text{Now,} \quad K_c=\frac{X^2}{(a-X)(b-X)}=\frac{(66{\cdot}5)^2}{(100-66{\cdot}5)^2}=4{\cdot}32.$$

$\because \quad a=b=100.$

(i) When 1 mole of acetic acid reacts with 0·5 mole of ethyl alcohol.

$$4{\cdot}32=\frac{X^2}{(1-X)(0{\cdot}5-X)} \quad \text{or,} \quad 6{\cdot}64X^2-12{\cdot}96X+4{\cdot}32=0$$

or, $X=0{\cdot}432.$

$$\text{(ii)} \quad 4{\cdot}32=\frac{X^2}{(1-X)(4-X)} \qquad \text{or,} \quad X=0{\cdot}930.$$

$$\text{(iii)} \quad 4{\cdot}32=\frac{X^2}{(1-X)(8-X)} \qquad \text{or,} \quad X=0{\cdot}967.$$

5. If a mixture of 3 moles of H_2 to 1 mole of N_2 react under a constant pressure of 100 atms to form at equilibrium 0·5 mole ammonia, calculate K_p.

From the equation, $\frac{1}{2} N_2+\frac{3}{2}H_2\rightleftharpoons NH_3$,

0·5 mole N_2 and 1·5 mole H_2 disappear for the formation of every single mole of NH_3. Therefore, 0·25 mole N_2 and 0·75 mole H_2 are to disappear for the formation of 0·5 mole NH_3.

So, $1-0{\cdot}25=0{\cdot}75$ mole N_2;

$3-0{\cdot}75=2{\cdot}25$ moles of H_2 and 0·5 mole NH_3, are present at the equilibrium.

Total number of moles of the mixture at equilibrium equals $0{\cdot}75+2{\cdot}25+0{\cdot}5=3{\cdot}5$.

Mole fraction of $N_2=\frac{0{\cdot}75}{3{\cdot}5}$, of $H_2=\frac{2{\cdot}25}{3{\cdot}5}$ and of $NH_3=\frac{0{\cdot}5}{3{\cdot}5}$.

Substituting these values in the expression,

$$K_p=\frac{X_{NH_3}P}{\left(X_{N_2}P\right)^{\frac{1}{2}}\left(X_{H_2}.P\right)^{\frac{3}{2}}}=\frac{\frac{0{\cdot}5}{3{\cdot}5}\times 100}{\left(\frac{0{\cdot}75}{3{\cdot}5}\times 100\right)^{\frac{1}{2}}\left(\frac{2{\cdot}25}{3{\cdot}5}\times 100\right)^{\frac{3}{2}}}$$

$$=5{\cdot}98\times 10^{-3}\ \text{atm}^{-1}.$$

Where, X_{NH_3} = mole fraction of NH_3; X_{N_2} = mole fraction of N_2; X_{H_2} = mole fraction of H_2 and P = total pressure.

6. A vessel contains ozone and oxygen at equilibrium with equilibrium constant in terms of partial pressures $=4{\cdot}0\times 10^{12}$ for the homogeneous reversible reaction, $2O_3\rightleftharpoons 3O_2$. If the mixture contains O_3 and O_2 in the molar proportion 1 : 980, what are the partial pressures of O_3 and O_2 in the equilibrium state ?

We have, $K_p=\frac{p^3_{O_2}}{p^2_{O_3}}=4{\cdot}0\times 10^{12}$

As partial pressure of a gas is directly proportional to the number of moles of that gas,

$$\frac{p_{O_3}}{p_{O_2}}=\frac{1}{980}\quad \text{or,}\quad p_{O_2}=980\,p_{O_3}$$

$$\text{or,}\quad 4\times 10^{12}=\frac{(980\,p_{O_3})^3}{p^2_{O_3}}=\frac{(980)^3\,p^3_{O_3}}{p^2_{O_3}}=(980)^3 p_{O_3}.$$

$$\therefore \quad p_{O_3}=\frac{4\times10^{12}}{(980)^3}=\frac{4\times10^{12}}{(98)^3(10)^3}=\frac{4\times10^9}{(98)^3}=4{\cdot}2\times10^3 \text{ atm.}$$

$$p_{O_2}=980\times4{\cdot}2\times10^3=4116\times10^3=41{\cdot}16\times10^5 \text{ atm.}$$

7. The equilibrium constant for the homogeneous reversible reaction, $2SO_3(g)\rightleftharpoons 2SO_2(g)+O_2\ (g)$, in terms of partial pressures is $32{\cdot}25\times10^{-2}$ at 300°A. What is its equilibrium constant in terms of concentration at the same temperature ?

We have, $K_p=K_c(RT)^{\Delta n}$ or, $32{\cdot}25\times10^{-2}=K_c(RT)^{\Delta n}$

or, $32{\cdot}25\times10^{-2}=K_c(0{\cdot}0821\times300)^{\Delta n}$

or, $K_c=\dfrac{32{\cdot}25\times10^{-2}}{(0{\cdot}0821\times300)^{\Delta n}}$ $\because$ $\Delta n=3-2=1$

$$\therefore \quad K_c=\frac{32{\cdot}25\times10^{-2}}{0{\cdot}0821\times300}=\frac{3{\cdot}25\times10^{-3}}{0{\cdot}821\times3}=1{\cdot}319\times10^{-3}.$$

8. PCl_5 is 80% dissociated at 250°C. Find its vapour density at that temperature. $(P=31)$;

Ranchi University, 1969, '74, '77.

$\alpha=\dfrac{80}{100}=0{\cdot}8=$ degree of dissociation.

$\alpha=\dfrac{d_0-d}{(n-1)d}$; $d_0=\dfrac{\text{Molecular weight of } PCl_5}{2}$

=true vapour density ;

d = vopour density at 250°C ; $n=2$ for the reaction,

$$PCl_5\rightleftharpoons PCl_3+Cl_2.$$

$$\therefore \quad 0{\cdot}8=\frac{\frac{1}{2}(31+35{\cdot}5\times5)-d}{d}=\frac{104{\cdot}25-d}{d}$$

or, $0{\cdot}8\times d=104{\cdot}25-d$ or, $d+0{\cdot}8d=104{\cdot}25$

or, $d=\dfrac{104{\cdot}25}{1{\cdot}8}=57{\cdot}916.$

9. $13{\cdot}5$ cc of HI is produced from the interaction of $8{\cdot}1$ cc of H_2 and $9{\cdot}3$ cc of I_2 vapour at 444°C. Calculate the equilibrium constant at this temperature.

Magadh University (Bihar) 1963, 66A ; Patna U. 1966A.

$H_2+I_2\rightleftharpoons 2HI$

1cc 1cc 2cc (at the same temperature and pressure)

1 mole 1mole 2 mole (according to Avogadro's hypothesis)

Or, $\frac{1}{2}$ mole $\frac{1}{2}$ mole 1 mole

i.e., $\frac{1}{2}$ cc $\frac{1}{2}$ cc 1 cc

Or, 6·75cc 6·75 cc 13·50 cc (according to the question)

$$\therefore \quad K_c = \frac{\frac{13\cdot50}{17\cdot40} \times \frac{13\cdot50}{17\cdot40}}{\frac{1\cdot35}{17\cdot40} \times \frac{2\cdot55}{17\cdot40}} = \frac{182\cdot25}{3\cdot4425} = 52\cdot941$$

$\because$ total volume $= 1\cdot35 + 2\cdot55 + 13\cdot5 = 17\cdot40$ cc.

10. Phosphorous pentachloride dissociates as, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ at 200°C. Calculate the equilibrium constant in terms of partial pressures, when 5 gm Cl_2 and 11 gm PCl_5 were found to be present per litre in equilibrium. ($R = 0\cdot082$ lit. atm. deg^{-1}. $mole^{-1}$).

Number of moles of chlorine/litre = Number of moles of PCl_3 /litre (according to recation) $= \frac{5}{71} = 0\cdot0704$ $\because$ Mol. wt. of $Cl_2 = 71$.

Number of moles of PCl_5 left undecomposed/litre $= \frac{11}{208\cdot5}$ $= 0\cdot0527$

$\because$ Mol. wt. of $PCl_5 = 31 + 35\cdot5 \times 5 = 208\cdot5$ $\because$ At. wt. of $P = 31$.

K_c (equilibrium constant in terms of concentrations)

$$= \frac{0\cdot0704 \times 0\cdot0704}{0\cdot0527}$$

$= 940\cdot4478$. We have, $K_p = K_c\,(RT)^{\Delta n}$.

$K = 940\cdot4478 \times (0\cdot082 \times 473) = 1590$ atms.

$\because \quad \Delta n = 0\cdot0704 + 0\cdot0704 - 1\cdot0527 = 0\cdot0881$;

$T = 273 + 200 = 473$°A.

Dissociation reaction follows the equation, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

11. Phosphorous pentachloride dissociates as, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Calculate the number of moles of chlorine produced when two moles of PCl_5 are heated at 250°C in a vessel of two litre capacity. The equilibrium constant of the reaction at 250°C is 0·041. *Bombay University I. Sc. 1976.*

$$\underset{2-2\alpha}{PCl_5} \rightleftharpoons \underset{2\alpha}{PCl_3} + \underset{2\alpha}{Cl_2}\,; \quad \alpha = \text{Degree of dissociation.}$$

Number of moles of PCl_3 per litre = Number of moles of Cl_2 per litre $=\frac{2\alpha}{2}=\alpha$.

Number of moles of undissociated PCl_5/litre $=\frac{2-2\alpha}{2}=1-\alpha$.

$$K_c=\frac{\alpha.\alpha}{1-\alpha}=\frac{\alpha^2}{1-\alpha} \text{ or, } 0{\cdot}041=\frac{\alpha^2}{1-\alpha} \text{ or, } \alpha^2=0{\cdot}041.$$

∵ α is neglected as compared to unity.

∴ $\alpha=0{\cdot}202$ = number of moles of Cl_2/litre.

12. At what pressure is only 1·0% I_2 not dissociated to atoms at 800°C if $K_p=1{\cdot}060\times10^{-2}$ atm for the reaction $I_2(g)\rightleftharpoons 2I(g)$?

If 1·0% is not dissociated, $\alpha=0{\cdot}99$ = degree of dissociation.

$$K_p=\frac{\left(\frac{2\alpha}{1+\alpha}P\right)^2}{\frac{1-\alpha}{1+\alpha}P} \quad ∵ \quad \underset{1-\alpha}{I_{2(g)}} \rightleftharpoons \underset{2\alpha}{2I_{(g)}}$$, products are indistinguishable.

Or, $K_p=\frac{4\alpha^2}{1-\alpha^2}P$ Or, $P=\frac{1-\alpha^2}{4\alpha^2}K_p$

$$=\frac{1-0{\cdot}9801}{4\times0{\cdot}9801}\times1{\cdot}06\times10^{-2}.$$

∴ $K=5{\cdot}38\times10^{-5}$ atms.

13. At elevated temperature gaseous iodine dissociates into atoms to such an extent that apparent pressure P deviates measurably from expected pressure P_0. If the total pressure difference is due to dissociation, calculate K_p for the process $I_{2(g)}\rightleftharpoons 2I_{(g)}$ at 800°C if $P_0=0{\cdot}3153$ atm and if $P=0{\cdot}3429$ atm.

Since pressure is directly proportional to the number of free particles at definite volume and temperature, $\frac{P_0}{P}=\frac{1}{1+\alpha}$. Where, P_0 = the pressure exerted by the system had there been no dissociation ; P = the pressure exerted by the system had there been dissociation and α = degree of dissociation.

$$\underset{1-\alpha}{I_{2(g)}} \rightleftharpoons \underset{2\alpha}{2I_{(g)}} \qquad \therefore \; \frac{P_0}{P} = \frac{1}{1-\alpha+2\alpha}$$

$$= \frac{1}{1+\alpha} \qquad \text{Or,} \;\; \alpha = \frac{P-P_0}{P_0}.$$

$$\text{Now, } K_p = \frac{\left(\frac{2\alpha}{1+\alpha}P\right)^2}{\frac{1-\alpha}{1+\alpha}P} = \frac{4\alpha^2}{1-\alpha^2}P$$

$$= \frac{4\left(\frac{P-P_0}{P_0}\right)^2 P}{1-\left(\frac{P-P_0}{P_0}\right)^2} = \frac{\{2(P-P_0)\}^2}{2P_0-P}$$

$$= \frac{(2\times 0{\cdot}0276)^2}{0{\cdot}2877} = 1{\cdot}06\times 10^{-2} \text{ atm.}$$

14. A mixture of SO_2 ann O_2 in the molar ratio 2 : 1 was kept over platinum catalyst in a reaction vessel at 650°C, the total pressure at equilibrium being found to be 10 atms. If 60% of SO_2 be converted to SO_3 in this reaction, calculate the equilibrium constant (K_p) for the reaction.

Calcutta University B.Sc. 1973.

$\underset{2-2\alpha}{2SO_2} + \underset{1-\alpha}{O_2} \rightleftharpoons \underset{2\alpha}{2SO_3}$ Where, α = degree of dissociation ; total number of moles $= 2-2\alpha+1-\alpha+2\alpha = 3-\alpha$ and P = total pressure.

$$K_p = \frac{\left(\frac{2\alpha}{3-\alpha}P\right)^2}{\left(\frac{2-2\alpha}{3-\alpha}P\right)^2\left(\frac{1-\alpha}{3-\alpha}P\right)} = \frac{2\alpha^2(3-\alpha)}{(1-\alpha)^2P}$$

$$= \frac{2\times 0{\cdot}6\times 0{\cdot}6\times(3-0{\cdot}6)}{(1-0{\cdot}6)(1-0{\cdot}6)\times 10} = 1{\cdot}08 \text{ mole. atm.}^{-1} \quad \because \; \alpha = \frac{60}{100} = 0{\cdot}6.$$

15. In a mixture of 1 part of N_2 to 3 parts of H_2, the mole percent of NH_3 at equilibrium was found to be 1·20 at 500°C at total pressure of 10 atms. Calculate the pressure at which the equilibrium mixture at this temperature contains 10·4 mole per cent of NH_3.

Let $^{x}NH_3$ = mole fraction of NH_3.

$$\left[\because \quad \frac{^{n}NH_3}{^{n}N_2+{}^{n}H_2+{}^{n}NH} = {}^{x}NH_3\right]$$

$$\therefore \quad {}^{x}NH_3\ 100 = 1{\cdot}2 \quad \text{or} \quad {}^{x}NH_3 = \frac{1{\cdot}2}{100} = 0{\cdot}012.$$

Now, $^{x}H_2 = \frac{3}{4}(1-0{\cdot}012)$ and $^{x}N_2 = \frac{1}{4}(1-0{\cdot}012)$.

$\because$ N_2 and H_2 are in 1 : 3 mole proportion ; the sum of mole fractions of N_2, H_2 and NH_3 is unity.

For the reaction; $N_2+3H_2 \rightleftharpoons 2NH_3$;

$$K_p = \frac{(x_{NH_3}P)^2}{(x_{N_2}.P)(x_{H_2}.P)^3}$$

$$= \frac{(0{\cdot}012\times10)^2}{\frac{1}{4}(1-0{\cdot}012)\times10\times\{\frac{3}{4}(1-0{\cdot}012)\times10\}^3}$$

$$= 1{\cdot}43\times10^{-5}\ \text{mole. atm}^{-2} \qquad \because\ P = 10\ \text{atms.}$$

Again, $100x'_{NH_3} = 10{\cdot}4 \quad \therefore \quad x'_{NH_3} = 0{\cdot}1.$

$$1{\cdot}43\times10^{-5} = \frac{(0{\cdot}1\times p')^2}{\frac{1}{4}(1-0{\cdot}1)p'\times\{\frac{3}{4}(1-0{\cdot}1)p'\}^3} \quad \therefore\ p' = 105\ \text{atms.}$$

16. When N_2 and H_2 are mixed in the proportion 1 : 3 at 50 atm. pressure and 650°C, the equilibrium concentration of ammonia is 25% by weight. Calculate the equilibrium constant.

Calcutta. U. B. Sc. 1969.

We have, $N_2+3H_2 \rightleftharpoons 2NH_3$. We therefore see (14×2) parts of N_2 by weight react with (3×2) parts of H_2 by weight to form ammonia in the reaction i.e., in $(28+6)$ parts by weight of the mixture of N_2 and H_2 there are 28 parts of N_2 by wt. and 6 parts of H_2 by wt. Therefore in 100 parts by weight of the mixture there are

$N_2 = \frac{28}{34}(100-25) = \frac{28}{34}\times75 = 61{\cdot}764\%$ by wt ; $H_2 = \frac{6}{34}(100-25) = \frac{6}{34}\times75 = 13{\cdot}235\%$ by wt and $NH_3 = 25\%$ by wt (according to the question). The percentages by wt expressed in terms of number of moles are given as $N_2 = \frac{61{\cdot}764}{28} = 2{\cdot}206$; $H_2 = \frac{13{\cdot}235}{2}$ $= 6{\cdot}617$ and $NH_3 = \frac{25}{17} = 1{\cdot}470$.

The mole fraction of $N_2 = \frac{2{\cdot}206}{2{\cdot}206 + 6{\cdot}617 + 1{\cdot}470} = \frac{2{\cdot}206}{10{\cdot}293}$.

The mole fraction of $H_2 = \frac{6{\cdot}617}{10{\cdot}293}$. The mole fraction of NH_3 $= \frac{1{\cdot}470}{10{\cdot}293}$. Substituting these values of mole fractions in the expression,

$$Kp = \frac{p^2_{\mathrm{NH_3}}}{p_{\mathrm{N_2}} \cdot p^3_{\mathrm{H_2}}} = \frac{\left(\frac{1{\cdot}470}{10{\cdot}293} \times 50\right)^2}{\frac{2{\cdot}206}{10{\cdot}293} \times 50 \left(\frac{6{\cdot}617}{10{\cdot}293} \times 50\right)^3}$$

$\because$ $p =$ mol. fraction x total pressure.

$K_p = 9{\cdot}48 \times 10^{-4}$ mole^{-2} atm^{-2}. at 650°C.

17. 4·5 gms of PCl_5 (molecular weight = 208·5) were completely vaporised at 250°C and the vapour occupied 1·7 litres at one atm. Calculate the degree of dissociation and the equilibrium constant of PCl_5 at this temperature.

Calcutta. U. 1963. B.Sc. ; Agra. U. 1966.

We have, $PV = \frac{W}{M}(1+\alpha)RT$. Given, $P = 1$ atm ; $V = 1{\cdot}7$ lits ; $W = 4{\cdot}5$ gms ; $M = 208{\cdot}5$; $T = 250 + 273 = 523$°A and $R = 0{\cdot}0821$ lit. atm/deg/mole (known).

$$\therefore \quad 1 \times 1{\cdot}7 = \frac{4{\cdot}5}{208{\cdot}5}(1+\alpha) \times 0{\cdot}0821 \times 523 \quad \text{or,} \quad \alpha = 0{\cdot}8356.$$

Now, $K_p = \frac{\alpha^2 P}{1-\alpha^2}$ for PCl_5 dissociation.

$$\therefore \quad K_p = \frac{(0{\cdot}8356)^2 \times 1}{1-(0{\cdot}8356)^2} = 2{\cdot}315.$$

18. 0·492 gm of nitrogen tetroxide occupies 241 ml at 65°C and 753 mm. Calculate the apparent molecular weight and the degree of dissociation. *Lucknow. U. 1961.*

We have, $PV = \frac{W}{M}(1+\alpha)RT$. $\frac{753}{760} \times \frac{241}{1000} = \frac{0{\cdot}492}{M}(1+\alpha)$

$$\times 0{\cdot}0821 \times 338$$

$\therefore$ $\alpha = 0{\cdot}608$. Degree of dissociation $= 60{\cdot}8\%$.

$\alpha = \dfrac{d_0 - d}{(n-1)d}$ for the reaction $N_2O_4 \rightleftharpoons 2NO_2$.

$$0{\cdot}608 = \frac{\frac{M_0}{2} - \frac{M}{2}}{(2-1)\frac{M}{2}} \quad \because \text{ Vap. density} = \frac{M}{2}.$$

Or, $0{\cdot}608 = \dfrac{M_0 - M}{M} = \dfrac{92 - M}{M}$ $\therefore$ $M = 57{\cdot}2$. Apparent mol. wt $= 57{\cdot}2$.

19. 480 ml N_2O_4 in a diffusion tube enclosed in a steam jacket is exposed to air. It is noted that the tube contains 700 ml of air at 100°C. Calculate the degree of dissociation.
[Vapour density of air $= 14{\cdot}41$]

We have from Graham's law of diffusion,

$$\frac{R_1}{R_2} = \frac{V_1}{V_2} = \sqrt{\frac{D_2}{D_1}}.$$

Time for diffusion is supposed to be same i.e., $t_1 = t_2$.

Where, R_1 = rate of diffusion of N_2O_4 ; R_2 = rate of diffusion of air ; V_1 = Volume of N_2O_4 diffused ; V_2 = Volume of air diffused ; D_1 = Vapour density of N_2O_4 and D_2 = Vapour density of air.

$$\frac{V_1}{V_2} = \sqrt{\frac{D_2}{D_1}} \quad \text{Or,} \quad \left(\frac{V_1}{V_2}\right)^2 = \frac{D_2}{D_1} \quad \text{Or,} \quad D_1 = \left(\frac{V_2}{V_1}\right)^2 . D_2$$

Or, $D_1 = \left(\dfrac{700}{480}\right)^2 . 14{\cdot}41 = 30{\cdot}64$.

Now, $\alpha = \dfrac{D_0 - D_1}{(n-1)D_1} = \dfrac{46 - 30{\cdot}64}{(2-1)30{\cdot}64}$ $\because$ $D_0 = \dfrac{92}{2} = 46$.

Or, $\alpha = 0{\cdot}5013$. Degree of dissociation $= 50{\cdot}13\%$

$\because$ true molecular weight of $N_2O_4 = 92$.

Problems for practice :

1. For an equilibrium reaction, the rate constant for the forward reaction and the backward reaction is $2{\cdot}38 \times 10^{-4}$ and $8{\cdot}15 \times 10^{-5}$ respectively. The equilibrium constant for this reaction will be (a) 0·34 ; (b) 3·42 ; (c) 2·92 ; (d) 0·292 ; (e) none of the above.

2. $A_{(i)}+B_{(i)} \rightleftharpoons C_{(i)}+H_{(i)}$. One mole of A and one mole of *B* are mixed in a volume of one litre. If 0·9 mole per litre of C is found at equilibrium, the equilibrium constant *K* is

(a) $\frac{(0{\cdot}9)\times(0{\cdot}1)}{(0{\cdot}9)\times(0{\cdot}1)}$; (b) $\frac{(0{\cdot}9)\times(0{\cdot}9)}{(0{\cdot}1)\times(0{\cdot}1)}$;

(c) $\frac{(0{\cdot}9)\times(1)}{(0{\cdot}1)\times(0{\cdot}9)}$; (d) $\frac{(0{\cdot}1)\times(0{\cdot}9)}{(0{\cdot}9)\times(1)}$.

3. 1·588 gms of N_2O_4 gives a total pressure of 760 mm when partially dissociated in a 500ml glass vessel at 25°C, what is the degree of dissociation ? (a) 0·184 ; (b) 0·648 ; (c) 0·514 ; (d) 0·43.

4. Under equilibrium conditions the amount of *HI* in a 3 litre vessel was 12·8 gms. Its equilibrium concentration is (a) 4·267 moles/litre ; (b) 0·033 mole/litre ; (c) 0·1 mole/litre ; (d) none of the above three values.

5. 2 gms of NH_4Cl are heated in one litre flask to 300°C. From the measurement of pressure it was found that 98% of NH_4Cl was dissociated. If to this flask 2 gms of dry ammonia is added, what would be the percentage of dissociation ? [Hints : Using $PV=\frac{W}{M}(1+\alpha)RT$, find out *P*. Knowing *P*, calculate K_p. Then try to find out new value of α, adding number of moles of dry ammonia (2gms). Ans. 86·2%]

6. When 1 mole of ethyl alcohol reacts with 1 mole of acetic acid, $\frac{2}{3}$ mole of ethyl acetate is formed. Determine the amount of ester present at equilibrium when (a) 3 moles of alcohol react with 1 mole of acid (b) one mole of alcohol reacts with 1 mole of acid in presence of 1 mole of water. Ans. 0·903 ; 0·542. *Cuttack 1962.*

7. Given that the degree of dissociation of PCl_5 at 523°*A* under atmospheric pressure is 0·978, calculate the values of K_p and K_c. *Allahabad.* U. *1967* Ans. 22·232 atm ; 0·517 lit^{-1}.

8. Calculate the dissociation constant of the reaction $2CO_2 \rightleftharpoons 2CO+O_2$ if the degree of dissociation of CO_2 at 1 atm is 40%. *Kurukshetra. U. 1971.* Ans. 0·074.

9. The equilibrium reaction between CO and steam is, $CO+H_2O \rightleftharpoons CO_2+H_2$. The equilibrium constant for this reaction is 4·38 at a certain temperature. If 100 moles of each of CO and steam are heated, find the composition of the mixture at equilibrium. *A*ns. CO_2=67·67 moles ; H_2=67·67 moles ; CO=32·33 moles ; H_2O=32·33 moles.

10. The equilibrium constant for the reaction, $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$, in terms of pressure is 3·1 at 1860°C. What is its equilibrium constant in terms of concentration at the same temperature ? Ans. $K_c=542{\cdot}2$.

11. The degree of dissociation of PCl_5 is 0·633 under a pressure of 3 atms. What must be the pressure if the dissociation is to be 80% ? Ans. 1·1282 atms.

12. At 800°C a vessel of 2 litres contains 0·433 mole of NH_3, 0·932 mole of N_2 and 0·993 mole of H_2 at equilibrium. Calculate the equilibrium constant in terms of concentration for the reaction, $2NH_3 \rightleftharpoons N_2+3H_2$. Ans. 1·2168.

13. A reaction of hydrogen and iodine is carried out by heating 60cc of hydrogen with 42cc of iodine in a closed vessel. At the equilibrium it is noted that the vessel contains 28cc of hydroiodic acid. Calculate the degree of dissociation of hydroiodic acid. Ans. 0·8815.

14. The equilibrium constant of the dissociation reaction, $PCl_5 \rightleftharpoons PCl_3+Cl_2$, is 2×10^{-2} at 250°C. Calculate the amount of chlorine present in a vessel of capacity 2 litres which contained 10 gms of PCl_5 initially. Ans. 0·0033 gm mole/lit.

15. In the dissociation of HI, it is found that 20% of the acid is dissociated when equilibrium is reached. *C*alculate the equilibrium constant in terms of pressure. Ans. $1{\cdot}5625\times10^{-2}$.

16. At 2155°*C* and 1 atm, steam is 1·18% decomposed into H_2 and O_2. *C*alculate K*p* at this temperature. *Calcutta*. U. *1971*. B. Sc. Ans. 8×10^{-7}.

17. A gm mole of a gas PQ. which is dissociated to an extent of 10%. at 127°*C* according to $PQ \rightleftharpoons P+Q$ occupies a volume

4×14^4cc. Calculate the total pressure at this temperature assuming the gases to be perfect. Ans. 0·235 atm.

18. 0·1 mole of H_2 and 0·2 mole of CO_2 are introduced in a vacuum flask at 450°*C*. The reaction, $H_2+CO_2\rightleftharpoons H_2O+CO$, occurs and at equilibrium the pressure is 0·5 atm. Analysis of the mixture shows that it contains 10 mole per cent of steam. Find the equilibrium constant at 450°*C*. Ans. 0·012016.

19. At 70°C and under atmospheric pressure N_2O_4 is 66% dissociated into NO_2. What volume will 10 gms of N_2O_4 occupy under these conditions? *Ranchi*. U. *1972*. Ans. 5·075 lit.

20. Discuss qualitatively the effect of temperature and pressure on the following chemical equilibria :

(i) $N_2+O_2\rightleftharpoons 2NO-43$K cals ; (ii) $N_2+3H_2\rightleftharpoons 2NH_3+22$ K cals.

Magadh. U. 1971, '73, '76 ; Calcutta. U. B. Sc. 1971 ; Venkateswara. U. *1971* ; *Hyderabad 1974*, '77.

[Hint : Heat of absorption = 43 K cals ; heat of evolution = − 22 K cals]

21. Formulate the equilibrium constant K*p* for the following dissociation equilibria, arrived at by starting from the pure reacion only, in terms of the total pressure P and the degree of dissociation α at equilibrium :

$COCl_2(g)\rightleftharpoons CO(g)+Cl_2(g)$; $2H_2S\rightleftharpoons 2H_2(g)+S_2(g)$.

Calcutta. U. *B.Sc. 1972*

22. Discuss the effects of pressure and temperature on the following chemical equilibria : (i) $2SO_2+O_2\rightleftharpoons 2SO_3+45{\cdot}2$ K cals, (ii) $H_2+I_2\rightleftharpoons 2HI-12{\cdot}0$ K cals. *Calcutta*. U. *B.Sc. 1973* ; *Hyderabad 1974*.

23. For the gaseous reaction $2SO_2+O_2\rightleftharpoons 2SO_3$, state whether the equilibrium will be disturbed and if so, in which direction, when : (i) the volume of the reaction vessel is increased at constant temperature ; (ii) SO_3 is some how removed from the vessel at constant volume and temperature and (iii) the reaction vessel is suddenly cooled. Briefly indicate reasons for your answers.

24. At 3000°A and 1 atm. pressure CO_2 is 40% dissociated into CO and O_2. Calculate K_p at this temperature.
Calcutta. U. *1974. B.Sc.* Ans. $2{\cdot}722 \times 10^{-1}$.

25. Calculate Kp for the reaction: $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g)$; if at 350°C and 50 atm. pressure 25·11 mole per cent of NH_3 be formed from a starting mixture of N_2 and H_2 in the ratio 1 : 3. *Calcutta.* U. *B.Sc. 1975.* Ans. $2{\cdot}76 \times 10^{-2}$.

26. 0·60 mole of ethyl acetate is produced at equilibrium, starting from 1 mole of each of pure ethyl alcohol and acetic acid. Calculate K_c and the amount of ester produced at equilibrium, starting from 0·1 mole acid, 0·2 mole alcohol and 0·1 mole water. *Calcutta.* U. *B.Sc.* 1976. Ans. 2·25 ; 0·12 mole.

27. At a total pressure of 1 atm and at 184°C, NO_2 is 5% decomposed according to the equation :
$2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$. Calculate K for this equilibrium.
Calcutta. U. *B.Sc. 1977*. Ans. $6{\cdot}757 \times 10^{-5}$.

28. At 500°C and 10 atm. pressure, a mixture of 1 part N_2 and 3 parts H_2, yields at equilibrium 1·20 mole percent NH_3. Calculate K_p for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$. *Calcutta.* U. *B. Sc. 1978.* Ans. 1.433×10^{-5}.

29. In the reaction, $H_{2(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{(g)}$, 0·10 mole of H_2 and 0·20 mole of I_2 react so that only 20% of H_2 is transformed into HI. Calculate the weight of HI formed. I. I. T. (Gp. B) 1975. Ans. 5·12 gms.

30. Ammonia under a pressure of 15 atm at 27°C is heated to 347°C in a closed vessel in the presence of a catalyst. Under these conditions NH_3 is partially dissociated according to the equation : $2NH_3 \rightleftharpoons N_2 + 3H_2$. The vessel is such that the volume remains effectively constant where as the pressure increases to 50 atm. Calculate the percentage of NH_3 actually decomposed. *I.I.T.*(*gp.* A) 1970. Ans. 61·3%.

31. Berthollet found that when 1 mole of acetic acid was heated with 0·33 and 0·50 mole respectively of ethyl alcohol, the ester produced, in the two cases were 0·293 and 0·414 mole

respectively. Show that these results are in accord with the law of mass action. *Ranchi.* U. *1965A.* Ans. Show value of K, same in two cases.

32. When acetic acid and ethyl alcohol are mixed together in equivalent proportions, equilibrium is reached when two thirds of acid and alcohol are used up. How much ester will be present in the equilibrium mixture, if the reaction is started with 60 gms of acetic acid and 23 gms of ethyl alcohol ? *Patna.* U. *1963* A, '64 ; *Ranchi.* U. *1964 A* ; *'65A, '69A* ; *Magadh.* U. *1966 A*, '*70A*, '73S, '75S.

33. At 60°C the vapour density of nitrogen peroxide is 30·65 and at 100°C it is 25·7. Calculate the degree of dissociation of the gas at these temperatures and explain whether the dissociation is exothermic or endothermic. *Patna.* U. *1962 A* ; *Magadh.* U. *1967 A.* Ans. 0·508 ; 0·79.

34. The equilibrium constant of reaction between ethyl alcohol and acetic acid is 4. Calculate the yield of ethyl acetate when 2·3 gms of ethyl alcohol react with 6 gms of acetic acid. *Magadh.* U. *1969A.* Ans. 2·04 gms.

35. In the reaction $2SO_2+O_2 \rightleftharpoons 2SO_3$, the equilibrium mixture at 700°C contains 40% of SO_3 by weight. Calculate the equilibrium constant. *Patna.* U. *1967A.* Ans. 1·92.

36. 25cc of hydrogen and 18cc of iodine were allowed to react at 465°C and at equilibrium 30·8cc of hydrogen iodide was formed. Calculate the equilibrium constant of the reaction. *Magadh.* U. *1966A*, *1975A.* Ans. 38·01.

37. What is the composition of the mixture at the equilibrium when I gm mole of acetic acid is mixed with 8 gm mole alcohol and the mixture undergoes reaction according to the reversible reaction $CH_3COOH+C_2H_5OH \rightleftharpoons CH_3COOC_2H_5+H_2O$? Equilibrium constant is given, 4·41. *Ranchi.* U. *1964A.* Ans. 0·97 gm mole ethyl acetate ; 0·03 gm mole acetic acid ; ethyl alcohol 7·03 gm mole.

38. 18 gms of ethyl acetate are produced when 90 gms of acetic acid are heated with 69 gms of ethyl alcohol. Find out the amount of yield of ethyl acetate when 180 gm acetic acid

are heated with 46 gms of alcohol. *Magadh.* U. *1964A, 1975S* ; *Ranchi.* U. 1977. Ans. 79·464 gms [Temp is kept const]

39. A mixture of hydrogen and iodine vapour in the molecular proportion of 2 : 1 was heated at 445°C till the change represented by the eqn. $H_2 + I_2 \rightleftharpoons 2HI$ attained eqm. The eqm. const at this temp. is 0·02. Calculate the percentage of iodine converted into hydrogen iodide. *Patna.* U. *1966A* ; *Magadh.* U. *1975A.* Ans. 11·7.

40. In the beginning of the reaction $A + B \rightleftharpoons C + D$ at 25°C the number of gm moles of A and B were equal. At equilibrium it was found that the number of gm moles of D were twice the number of gm moles of A. Calculate the value of the eqm. const at 25°C. *Ranchi.* U. *1969A. Ans.* 4.

41. 25cc of H_2 and 18cc I_2 vapour were heated in a sealed tube at 465°C when at the eqm. 30·8 cc of HI was formed. Calculate the degree of dissociation of HI at 465°C. *Rajasthan* T. D. II *1962* ; *Agra 1973* ; *Meerut 1970.* Ans. 24·5%.

42. The equilibrium mixture at $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ exists at a definite temperature and pressure. The reaction is exothermic. Explain how the amount of the product will be affected by a change of temperature and pressure on the system. State the principle by which it can be explained. *W.B.H.S.C. 1979.*

43. An equilibrium mixture at 430°C was found to contain 0·60 mole of nitrogen, 0·4 mole of hydrogen and 0·14 mole of ammonia in a litre. Calculate the equilibrium constant for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$. *Calcutta.* U. *B.Sc. (A). 1979.* Ans. $0{\cdot}515\ \text{mole}^{-2}.\ \text{lit}^{2}$.

44. In a reaction of the type $A_2 + B_2 \rightleftharpoons 2(AB)$, there were produced at equilibrium at 45°C, 3·7 moles of (AB) from 2·06 moles of A_2 and 3·19 moles of B_2. Calculate the equilibrium constant. *Calcutta. U. B.Sc.* 1979. Ans. $0{\cdot}486 \times 10^{-2}$.

45. 10 gm molecules of HI were produced by the interaction of 15 gm. molecules of H_2 and 5·2 gm molecules of I_2 vapour at

444°C. Calculate the equilibrium constant of the reaction $H_2+I_2 \rightleftharpoons 2HI$. *Uttar Pradesh I.Sc. 1978.* Ans. 50.

46. The concentration of H_2, I_2 and HI at equilibrium in the reaction $H_2+I_2 \rightleftharpoons 2HI$ are 8, 3 and 28 moles per litre respectively. Calculate the equilibrium constant. *Uttar Pradesh I.Sc. 1977.* Ans. 32·67.

47. A gaseous mixture contains 1 gm per litre hydrogen and 2·8 gm/litre nitrogen. Find out the molar concentration of hydrogen and nitrogen in the mixture. Molecular weight of hydrogen is 2 and that of nitrogen is 28. *Uttar Pradesh 1977S.* Ans. 0·5 gm mole/litre ; 0·1 gm mole/litre.

48. In the reaction $PCl_5 \rightleftharpoons PCl_3+Cl_2-y$ cal. what changes in temperature and pressure would you introduce to decrease the the dissociation of PCl_5 ? *Uttar Pradesh 1978S. I.Sc.*

CHAPTER 4

Problems on percentage composition of the organic and inorganic compounds and their empirical and molecular formulae.

Percentage composition gives the proportion by volume or weight of each constituent present in 100 parts by volume or weight of the organic or inorganic compound.

Empirical formula expresses the simplest relative ratio of the atoms of each element present in one molecule of the compound. The empirical formula of a compound (organic or inorganic) is derived from its percentage composition in the following steps : (a) The percentage of each element present in the compound is divided by its atomic weight. The quotients thus calculated express the relative number of atoms of the elements. (b) Each quotient is then divided by the smallest quotient to get the simplest ratio between the atoms of the elements. (c) If the simplest ratio obtained above is fractional, it is multiplied througout by the smallest possible integer to obtain the simplest whole number ratio. This step is essential since atoms can be present only in whole numbers according to Dalton's atomic theory.

Molecular formula represents the actual number of atoms of each element present in a molecule of the compound (organic or inorganic).

Molecular formula $= n \times$ Empirical formula.

Where, $n =$ a simple whole number.

$$\text{or, } \frac{\text{Molecular formula}}{\text{Empirical formula}} = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = n$$

$$\text{or, } \frac{\text{Molecular formula}}{\text{Empirical formula}} = \frac{2 \times \text{Vapour density}}{\text{Empirical formula weight}} = n$$

$$\therefore \frac{2 \times \text{Vapour density of a compound}}{\text{Empirical formula weight of the compound}} = n.$$

Solved problems

1. Calculate the percentage of water of crystallisation in $MgSO_4.7H_2O$. *Bihar H.S. 1965.*

246 gm $MgSO_4.7H_2O$ contain 126 gm water of crystallisation $\therefore$ 100 gm $MgSO_4.7H_2O$ contain $\frac{126}{246} \times 100 = 51{\cdot}219$ gm water of crystallisation. $\because$ Mol. Wt. of $MgSO_4.7H_2O = 246$; mol. wt. of water $= 18$.

2. Percentage of water of crystallisation in $BaCl_2XH_2O$ was found to be 14·75%. Find the number of molecules of water, X in the compound. *Senior Cambridge, 1964.*

$(208+18X)$gm $BaCl_2XH_2O$ contain 18X gm water of crystallisation.

$\therefore$ 100 gm " " $\frac{18X}{208+18X}$ " "

$\frac{18X}{208+18X} = 14{\cdot}75$ by the question. $\therefore$ $X = 1{\cdot}998 \approxeq 2$.

3. The formula of blue vitriol is $CuSO_4nH_2O$. On heating one gram of this, a residue of constant weight, equal to 0·638 gm is obtained. Find the value of n. ($Cu=63{\cdot}5$, $S=32$, $O=16$) *West Bengal H.S. 1974.*

$(159{\cdot}5+18n)$ gm $CuSO_4nH_2O$ leave 159·5 gm residue.

$\therefore$ 1 " " leaves $\frac{159{\cdot}5}{159{\cdot}5+18n}$ gm "

$\frac{159{\cdot}5}{159{\cdot}5+18n}=0{\cdot}638$ by the question. $\therefore$ $n=5{\cdot}027\approxeq 5$.

4. Find the percentage composition of nitric acid molecule.

63 gm HNO_3 contain 1 gm hydrogen.

$\therefore$ 100 " " " $\frac{1}{63}\times 100$ " " . Percentage of $H=1{\cdot}587$.

63 gm HNO_3 contain 14 gm nitrogen.

$\therefore$ 100 " " " $\frac{14\times 100}{63}$ " .

Percentage of $N=22{\cdot}222$.

63 gm HNO_3 contain 48 gm oxygen.

$\therefore$ 100 gm " " $\frac{48\times 100}{63}$ gm " .

Percentage of $0=76{\cdot}190$.

5. An organic compound was found to contain carbon 77·42%, hydrogen 7·53% and nitrogen 15·05%. Its vapour density was found to be 46·5. Calculate its empirical and molecular formulae. *All India H. S. 1970.*

Calculation of empirical formula

Name of the element present in the compound	Percentage	Percentage/At.wt	Number obtained in the previous column / Smallest number obtd.	Simplest relative ratio of atoms
C (carbon)	77·42	$\frac{77{\cdot}42}{12}=6{\cdot}45$ At.wt. of C=12	$\frac{6{\cdot}45}{1{\cdot}075}=6$	6
H (hydrogen)	7·53	$\frac{7{\cdot}53}{1}=7{\cdot}53$ At. wt. of H=1	$\frac{7{\cdot}53}{1{\cdot}075}=7$	7
N (nitrogen)	15·05	$\frac{15{\cdot}05}{14}=1{\cdot}075$ At. wt. of N=14	$\frac{1{\cdot}075}{1{\cdot}075}=1$	1

Empirical formula of the organic compound is therefore C_6H_7N.

Calculation of molecular formula

Now, molecular formula $= n$(empirical formula).

Where, $n = a$ simple positive whole number.

or, $n = \dfrac{\text{Molecular weight}}{\text{Empirical formula weight}} = \dfrac{2 \times \text{Vapour density}}{\text{Empirical formula weight}}$

or, $n = \dfrac{2 \times 46{\cdot}5}{72+7+14} = 1$. $\therefore$ Molecular formula of the organic compound is C_6H_7N.

6. 0·275 gm of an organic compound on combustion gave 0·6540 gm of CO_2 and 0·3375 gm of H_2O ; its vapour density as referred to hydrogen as unity was 37. Find out its molecular formula. *Delhi. H. S.* 1971 ; *Magadh. U.* 1974*A*.

Percentage Composition

44 gm CO_2 contain 12 gm carbon
$\therefore$ 0·6540 „ „ „ $\frac{12}{44} \times 0{\cdot}6540$ „
18 gm H_2O contain 2 gm hydrogen
$\therefore$ 0·3375 „ „ „ $\frac{2}{18} \times 0{\cdot}3375$ „ .

0·275 gm of the organic compound contains $\frac{12}{44} \times 0{\cdot}6540 =$ 0·178 gm carbon and $\frac{2}{18} \times 0{\cdot}3375 = 0{\cdot}0375$ gm hydrogen.

$\therefore$ Percentage of carbon $= \dfrac{0{\cdot}178 \times 100}{0{\cdot}275} = 64{\cdot}727$; percentage of hydrogen $= \dfrac{0{\cdot}0375 \times 100}{0{\cdot}275} = 13{\cdot}636$ and percentage of oxygen $= 100 - (64{\cdot}727 + 13{\cdot}636) = 21{\cdot}637$.

It is assumed that the organic compound contains C, H and O as constituent elements.

Calculation of empirical formula

Name of the element present in the organic compound	Percentage	Percentage/At. wt	Number obtained in the column just before / Smallest number obtained	Simplest relative ratio of atoms
C (carbon)	64·727	$\frac{64{\cdot}727}{12} = 5{\cdot}393$	$\frac{5{\cdot}393}{1{\cdot}352} = 4$	4
H (hydrogen)	13 636	$\frac{13{\cdot}636}{1} = 13{\cdot}636$	$\frac{13{\cdot}636}{1{\cdot}352} = 10$	10
O (Oxygen)	21·637	$\frac{21{\cdot}637}{16} = 1{\cdot}352$	$\frac{1{\cdot}352}{1{\cdot}352} = 1$	1

Empirical formula of the organic compound is $C_4H_{10}O$.

Calculation of Molecular formula

Now, $n=\frac{2\times\text{vapour density}}{\text{Empirical formula weight}}=\frac{2\times37}{74}=1.$

Where, n = a simple positive whole number. $\therefore$ molecular formula of the organic compound is $C_4H_{10}O$. Structural formula is $C_2H_5OC_2H_5$ (diethyl ether).

7. Carbohydrates are compounds containing only carbon, hydrogen and oxygen having the atomic ratio of H : O as 2 : 1. When heated in absence of air, these compounds decompose to form carbon and water. (a) If 310 gms of a carbohydrate leave a residue of 124 gms of carbon on heating in absence of air, what is the empirical formula of the hydrocarbon ? (b) If 0·0833 mole of the carbohydrate contains 1 gm mole hydrogen, what is the molecular formula of the carbohydrate ? *I. I. T. 1969.*

(a) **percentage composition**

310 gm carbohydrates contain 124 gm carbon.

$\therefore$ 100 „ „ „ „ $\frac{124\times100}{310}=40$ „.

Percentage of C = 40.

310 gm carbohydrates produce $(310-124)=186$ gm water.

$\because$ 18 gmH_2O contain 2 gm hydrogen.

$\therefore$ 186 gm „ „ $\frac{2}{18}\times186=20{\cdot}66$ gm hydrogen.

Or, 310 gm carbohydrates contain 20·66 gm hydrogen.

$\therefore$ 100 „ „ „ $\frac{20{\cdot}66}{310}\times100=6{\cdot}7$ „.

Percentage of H = 6·7.

Or, percentage of $O=100-(40+6{\cdot}7)=53{\cdot}3$.

Calculation of empirical formula

Name of the element present in the compound	Percentage	Percentage/At.wt	Number obtained in the previous column/ Smallest number obtd.	Simplest relative ratio of atoms
C (carbon)	40	$\frac{40}{12}=3{\cdot}33$	$\frac{3{\cdot}33}{3{\cdot}33}=1$	1
H (hydrogen)	6·70	$\frac{6{\cdot}7}{1}=6{\cdot}70$	$\frac{6{\cdot}7}{3{\cdot}33}=2$	2
O (oxygen)	53·30	$\frac{53{\cdot}30}{16}=3{\cdot}33$	$\frac{3{\cdot}33}{3{\cdot}33}=1$	1

Empirical formula of the carbohydrate is therefore CH_2O.

(b) According to the question, 0·0833 mole carbohydrate contains 1 gm mole hydrogen.

Or, 0·0833 mole carbohydrate contains 2 gms of hydrogen.

Or, 1 „ „ „ $\frac{2}{0\cdot0833}$ = 24 gms. „

∴ one mole carbohydrate contains 24 atoms of hydrogen.

Where, 1 gm mole hydrogen = 2 gm hydrogen ; at wt. of H = 1. As the empirical formula gives the simplest relative ratio of atoms of C, H and O as 1 : 2 : 1, molecular formula of the carbohydrate is $C_{12}H_{24}O_{12}$.

8. A substance has the following percentage composition :—

N = 35% ; H = 5% ; 0 = 60%. On being heated it yielded a gas containing 63·7% N and 36·3% O. Calculate the formula of each substance and construct the equation representing the chemical change. *Ranchi. U. P. U. 1970.*

Empirical formula calculation

Name of the element present in the substance	Percentage	Percentage/ Atomic Weight	Number obtained in the previous column/ Smallest number obtd.	Simplest relative ratio of atoms
N (nitrogen)	35	$\frac{35}{14} = 2\cdot5$	$\frac{2\cdot5}{2\cdot5} = 1\times2 = 2$	2
H (hydrogen)	5	$\frac{5}{1} = 5$	$\frac{5}{2\cdot5} = 2\times2 = 4$	4
O (oxygen)	60	$\frac{60}{16} = 3\cdot75$	$\frac{3\cdot75}{2\cdot5} = 1\cdot5\times2 = 3$	3

Empirical formula of the substance is $N_2H_4O_3$. Probable molecular formula of the substance is NH_4NO_3.

Empirical formula calculation of the evolved gas

Name of the element present in the gas molecule	Percentage	Percentage/ At. Wt	Number obtained in the just before this column/ Smallest number obtd.	Simplest relative ratio of atoms
N (nitrogen)	63·7	$\frac{63\cdot7}{14} = 4\cdot550$	$\frac{4\cdot550}{2\cdot268} = 2$	2
O (oxygen)	36·3	$\frac{36\cdot3}{16} = 2\cdot268$	$\frac{2\cdot268}{2\cdot268} = 1$	1

Empirical formula of the evolved gas is N_2O. Probable molecular formula of the evolved gas is N_2O. Probable chemical equation representing the chemical change is given below.

$NH_4NO_3 \xrightarrow{\Delta} N_2O+2H_2O$. Δ is the symbol for heating.

9. A hydrate on being rendered anhydrous loses 45·6% of its weight. The anhydrous substance on analysis shows the following percentagecomposition : Al = 10·5%, K = 15·1%, S = 24·8% and O = 49·6%. What will be the empirical formula of the hydrate and the anhydrous substance ? *West Bengal H. S. 1975.*

Name of the element present in the hydrated substance and name of the compd.	Percentage	Percentage / At. wt or mol. wt.	Number obtained in the previous column / Smallest number obtd.	Simplest relative ratio of atoms or moles
Al (aluminium) element	10·5	$\frac{10{\cdot}5}{27}=0{\cdot}388$	$\frac{0{\cdot}388}{0{\cdot}387}=1\times2=2$	2
K (potassium) element	15·1	$\frac{15{\cdot}1}{39}=0{\cdot}387$	$\frac{0{\cdot}387}{0{\cdot}387}=1\times2=2$	2
S (sulphur) element	24·8	$\frac{24{\cdot}8}{32}=0{\cdot}775$	$\frac{0{\cdot}775}{0{\cdot}387}=2\times2=4$	4
O (oxygen) element	49·6	$\frac{49{\cdot}6}{16}=3{\cdot}100$	$\frac{3{\cdot}100}{0{\cdot}387}=8\times2=16$	16
H_2O (water) compound	45·6	$\frac{45{\cdot}6}{18}=2{\cdot}533$	$\frac{2{\cdot}533}{0{\cdot}387}=6{\cdot}54\times2=13$	13

The empirical formula of the hydrate is $Al_2K_2S_4O_{16}, 13H_2O$. The empirical formula of the anhydrous substance is $Al\ K_2\ S_4O_{16}$. Probable molecular formula of the hydrate is $Al_2(SO_4)_3, K_2SO_4, 13H_2O$.

10. A compound contains 37·8% carbon, 6·3% hydrogen and 55·9% of chlorine. 2·62 gms of this compound on vaporisation gives 624 ml of vapour at 100°C and 775 mm pressure. Determine the empirical formula and molecular formula. (Cl = 35·5) *West Bengal. H. S. Comp. 1975. Calculation of empirical formula.*

Name of the element present in the compound	Percentage	Percentage/ At. Wt.	Number obtained in the previous column/ Smallest number obtd.	Simplest relative ratio of atoms
C (carbon)	37·8	$\frac{37{\cdot}8}{12}=3{\cdot}15$	$\frac{3{\cdot}15}{1{\cdot}57}=2$	2
H (hydrogen)	6·3	$\frac{6{\cdot}3}{1}=6{\cdot}30$	$\frac{6{\cdot}30}{1{\cdot}57}=4$	4
Cl (chlorine)	55·9	$\frac{55{\cdot}9}{35{\cdot}5}=1{\cdot}57$	$\frac{1{\cdot}57}{1{\cdot}57}=1$	1

Empirical formula of the compound is C_2H_4Cl.

We have, $PV=\frac{W}{M}RT$ (Vide. Chapter 1). $\frac{775}{760}\times\frac{624}{1000}$ $=\frac{2{\cdot}62}{M}\times 0{\cdot}0821\times 373$. $\therefore$ $M=126{\cdot}089$. Molecular formula $=n$ (empirical formula).

Where, $n=a$ simple positive whole number.

$$\text{Now, } n=\frac{\text{molecular weight}}{\text{empirical formula weight}}=\frac{126{\cdot}089}{63{\cdot}500}=1{\cdot}985\approx 2.$$

$\therefore$ molecular formula of the compound is $C_4H_8Cl_2$.

11. A compound of carbon, hydrogen and nitrogen contains these elements in the ratio 9 : 1 : 3·5. Calculate its empirical formula. If its molecular weight is 108, what is its molecular formula? *I. I. T. (Group A) 1973.*

Name of the element present in the compound with proper symbol	Weight ratio	Weight ratio/ Atomic weight	Number obtd. in the column before this Smallest number obtd.	Simplest relative ratio of atoms
C (carbon)	9	$\frac{9}{12}=0{\cdot}75$	$\frac{0{\cdot}75}{0{\cdot}25}=3$	3
H (hydrogen)	1	$\frac{1}{1}=1$	$\frac{1}{0{\cdot}25}=4$	4
N (nitrogen)	3·5	$\frac{3{\cdot}5}{14}=0{\cdot}25$	$\frac{0{\cdot}25}{0{\cdot}25}=1$	1

The empirical formula of the compound is C_3H_4N.

Molecular formula $=n$ (empirical formula). Where, $n=a$ simple positive whole number.

$$\text{Again, } n=\frac{\text{molecular weight}}{\text{empirical formula weight}}=\frac{108}{54}=2.$$

$\therefore$ molecular formula of the compound is $C_6H_8N_2$.

12. Two oxides of a metal contain 27·6% oxygen and 30% oxygen respectively. If the formula of the first oxide be M_3O_4, find that of the second.

Let the atomic weight of M de X.

We have, $3M+2O_2=M_3O_4$.

3X gm M on reacting with oxygen to form (3X+64) gm M_3O_4.

Or, 1 ,, ,, ,, ,, ,, ,, ,, ,, $\frac{3X+64}{3X}$,, ,,

Or, 72·4 ,, ,, ,, ,, ,, ,, ,, ,, $\frac{(3X+64)72{\cdot}4}{3X}$ gm ,,

$\because$ in the first oxide,% of $M=100-27{\cdot}6=72{\cdot}4$.

$\therefore\quad \frac{(3X+64)72{\cdot}4}{3X}=100. \quad \therefore\quad X=55{\cdot}97.$

Empirical formula calculation of the second oxide :

Name of the element present in 2nd oxide.	Percentage	Percentage/ At. Wt.	Number obtained in the previous column/ smallest number obtd.	Simplest relative ratio of atoms
M (metal)	70	$\frac{70}{55{\cdot}97}=1{\cdot}25$	$\frac{1{\cdot}25}{1{\cdot}25}=1\times2=2$	2
O (oxygen)	30	$\frac{30}{16}=1{\cdot}875$	$\frac{1{\cdot}875}{1{\cdot}25}=1{\cdot}5\times2=3$	3

Empirical formula of the second oxide is M_2O_3.

13. A compound containing sodium, sulphur, oxygen and hydrogen gave on analysis the following results : Na=14·31% ; S=9·97% ; H=6·25% ; O=69·47%. Calculate the formula on the assumption that all the hydrogen in the compound is present in combination with oxygen as water of crystallisation. Molecular weight of the compound is 322. *M. U. 1969S* ; *Nagpur Pre. U. 1970* ; *Patna U. 1968.*

Name of the element present in the inorganic compound with proper symbol	Percentage	Percentage/ At. Wt.	Number obtained in the previous column/ smallest number obtd.	Simplest relative ratio of atoms
Na (sodium)	14·31	$\frac{14{\cdot}31}{23}=0{\cdot}622$	$\frac{0{\cdot}622}{0{\cdot}311}=2$	2
S (sulphur)	9·97	$\frac{9{\cdot}97}{32}=0{\cdot}311$	$\frac{0{\cdot}311}{0{\cdot}311}=1$	1
H (hydrogen)	6·25	$\frac{6{\cdot}25}{1}=6{\cdot}25$	$\frac{6{\cdot}25}{0{\cdot}311}=20$	20
O (oxygen)	69·47	$\frac{69{\cdot}47}{16}=4{\cdot}341$	$\frac{4{\cdot}341}{0{\cdot}311}=14$	14

Empirical formula of the inorganic compound is $Na_2SH_{20}O_{14}$.

[For more than 0·5 value, take next full number e. g ; $1{\cdot}6\simeq2$. For less than 0·5 value, take full number containing this value e.g ; 2·4≃2. For 0·5 value, make it full number by multiplying least full number e. g ; $1{\cdot}5\times2=3$]

Now, molecular formula$=n$ (empirical formula). Where, $n=$a simple positive whole number. Again,

$$n=\frac{\text{molecular wt}}{\text{empirical formula wt}}\quad \text{Or, } n=\frac{322}{46+32+20+16\times14}=\frac{322}{322}=1.$$

Molecular formula of the inorganic compound is $Na_2SH_{20}O_{14}$.

∴ molecular formula of the inorganic compound (assuming all the hydrogen in the compound, present in combination with oxygen as water of crystallisation) is $Na_2SO_4, 10H_2O$.

Preblems for practice :

1. Calculate the percentage of oxygen in heavy water. Ans. 80. D=2.

2. Calculate the percentage of crystallisation in sodium thiosulphate crystals ($Na_2S_2O_3.5H_2O$). *Senior Cambridge. 1967.* Ans. 32·29.

3. A hydrated sulphate of a divalent metal (at.wt. 24) contains 51·22% water of crystallisation. Calculate the number of molecules of water of crystallisation in the hydrated salt. *Bombay. U. 1968.* Ans. 7.

4. Blue vitriol is represented by the formula $CuSO_4.nH_2O$. One gram of the sample on being heated was reduced to a constant weight equal to 0·64 gm. Find the value of *n*. (At. Wt : Cu=63·5 ; S=32) *W.B.E. Adn. Test. E. 1974.* Ans. 4·984.

5. 1·5 gms of hydrated calcium chloride when heated left behind 0·76 gm of the anhydrous salt. Calculate the percentage of water present and also the number of molecules of water of crystallisation per one molecule of the anhydrous salt. Ans. 49·34% ; 6.

6. A metal X having an atomic weight of 197 yields a chloride containing 35·1% of chlorine. Calculate the simplest formula of the chloride. *Senior Cambridge. 1967.* Ans. XCl_3.

7. An organic compound has the following percentage composition C−60%, H−6·43%, N−10·09% rest−oxygen. Find its empirical formula. *W. B. E. Adn. T. E. 1970.* Ans. $C_7H_9NO_2$.

8. A certain compound containing only carbon and oxygen

has an approximate molecular weight of 290. On analysis it is found to contain 50% by weight of each element. What is the molecular formula of the compound ? *I. I. T. (Group A) 1970.* Ans. $C_{12}O_9$.

9. A gaseous compound of carbon and nitrogen containing 53·8% by weight of nitrogen was found to have vapour density of 25·8. What is the molecular formula of the compound ? *I. I. T. (Group A) 1971.* Ans. C_2N_2.

10. An organic compound was found to contain carbon 14·5%, hydrogen 1·8%, chlorine 64·46% and oxygen 19·24%. Its molecular weight was found to be 165·5. Calculate its empirical and molecular formula. *All India H. S. 1971.* Ans. $C_2H_3Cl_3O_2$.

11. An organic compound has the following percentage composition ; C = 40% ; H = 6·67% ; Oxygen by difference. Its vapour density is 15. Find the empirical and molecular formula of the compound. *Delhi. H. S. 1972.* Ans. CH_2O.

12. An organic compound contains 10·04% carbon, 89·12% chlorine and rest hydrogen. Find out the empirical formula of the compound ? *W. B. H. S. Tech. 1974.* Ans. $CHCl_3$.

13. A compound of carbon, hydrogen and oxygen contains 40%C, 6.6%H and the rest is oxygen. Its vapour density is 30. Find the molecular formula of the compound and write down the possible structural formula also. *W. B. E. Adn. T. E. 1975 ; Hyderabad I. Sc. 1977. Indian S. C. E. 1978.* Ans. $C_2H_4O_2$, CH_3COOH (acetic acid).

14. An organic compound containing C, H and O was subjected to combustion. From 1·367 gm of the substance were obtained 3·002 gm of CO_2 and 1·640 gm of H_2O. Find out the empirical formula. *I. I. T. (Group A). 1975.* Ans. C_3H_8O.

15. Carbon combines with hydrogen to form three compounds A, B and C. The percentages of hydrogen in A, B and C are 25%, 14·3% and 7·7% respectively. Find the empirical formula of the compounds. *I.I.T. (Group B). 1973.* Ans. CH_4, CH_2 and CH.

16. An organic compound on analysis gives the following result, carbon = 54·56 per cent, hydrogen = 9·06 per cent, oxygen

=36·38 percent. Its vapour density is 44. Calculate its molecular formula. *W.B.E. Adn. T.·E. 1973, '78.* Ans. $C_4H_8O_2$.

17. A compound (*X*) having the composition, Ca=40% ; C=12% ; O=48%, leaves on heating a residue (Y). (Y) has the following percentage composition : Ca=71·43% ; O=28·57%. Calculate the formula of (X) and (Y) and give the equation of the change by which (X) is transformed into (Y). Ans. X=$CaCO_3$, Y=CaO ; Eqn : $CaCO_3 \rightarrow CaO + O_2$.

18. A gaseous hydrocarbon contains 85·62% carbon, 14.38% hydrogen. The density of the gas 1·26 gm per litre. Determine the molecular formula of the hydrocarbon. *West. Bengal. H. S. Comp. 1974.* Ans. C_2H_4.

19. A compound contains 10·05% carbon, 0·84% hydrogen and 89·1% chlorine. Its density in the gaseous state at 150°C and 760 mm pressure is 3·43 gm/litre. What are its empirical formula and molecular formula ? *West. Bengal. H. S. 1976.* Ans. $CHCl_3$.

[Hints. Find out mol. wt. using $PV=\frac{W}{M}RT$ equation]

20. Calculate the formulae of the following compounds whose percentage composition by weight is given :

(a) K=56·28% ; C=8·69% ; O=34·73%

(b) C=54·67% ; H=9·11% ; O=36·22%

Hyderabad I. Sc. 1973. Ans. K_2CO_3 ; C_2H_4O.

21. The percentage composition of a compound is K=24·65% ; Mn=34·85% and O=40·5%. Find its empirical formula. If its molecular weight is 158, find its molecular formula. *Hyderabad I. Sc. 1975.* Ans. $KMnO_4$.

22. A compound of carbon, hydrogen and oxygen contains 40%C, 6·66%H and the rest is oxygen. Its vapour density is 45. Find the molecular formula of the compound. L. N. M. U. *1976 A.* Ans. $C_3H_6O_3$.

23. A metal forms two oxides A and B. A contains 30% and B contains 22·2% oxygen. If the formula of A is M_2O_3, find that of B. *Patna. U. 1975 A.* Ans. MO.

24. 0·15 gm of a liquid A when vaporised occupies 62·4 ml at 27°C and 750 mm pressure. A contains 40%C, 6·67%H and the

rest is oxygen. From these data determine the molecular formula of A. *Patna. U. 1963* ; *Magadh. U. 1963.* Ans. $C_2H_4O_2$.

25. A crystallised salt is mixed with sand and gives on analysis the following results ; Cu=22·905% ; S=11·52%, O=23·085% ; H_2O=32·463% and the rest sand. Deduce the percentage composition of the crystallised salt and write down its molecular formula. *Patna.* U. *1974.* Ans. $CuSO_4, 5H_2O$.

26. An organic compound contains 54·54%C, 9·1%H and 36·36%O. Find the empirical formula of the compound. 0·11 gm of the same compound on vaporisation displaced 20 ml of air at S. T. P. Find the molecular formula. *Indian School certificate Examination, 1978.* Ans. C_2H_4O ; $C_6H_{12}O_3$.

27. A substance contains 37·8%C, 6·3%H and 55·9% of Cl. When vaporised, 0·127 gm occupy a volume of 22·4ml at N. T. P. What is the molecular formula of the compound ? *W. B. J. E. E. 1977.* Ans. $C_4H_8Cl_2$.

28. A compound contains 37·8% carbon, 6·3% hydrogen and 55·9% of chlorine. 0·638 gm of the compound when vaporised occupies a volume of 154ml at 100°C and normal pressure. What is the molecular formula of the compound ? What is its exact molecular weight ? Cl=35·5 *W. B. H. S. C. 1979.* Ans. $C_4H_8Cl_2$; 126·86.

29. An organic compound was found to contain 62·07%C and 10·34%H and had a vapour density of 29. Calculate its molecular formula. *W. B. J. E. E. (Tc) 1979* Ans. C_3H_6O.

30. An organic compound contains 62% carbon, 10·4% hydrogen and the rest oxygen. Find the empirical formula of the compound. If the vapour density of the compound is 29, what is its molecular formula ? *I. S. C. E. 1979.* Ans. C_3H_6O.

31. An organic compound 'A' contains 40·68%C, 8·47%H, 23·73%N. Its molecular weight is 59. What is its molecular formula ? *Revisankar. U. 1977.* Ans. C_2H_5NO.

32. A volatile orgc. compd. has the following composition : C−10·00% ; H=0·85% and Cl=89·15%. 0·64 gm. of the compd. produces 121 cc. of its vapour at N.T.P. Find out the molecular formula of the compd. *Ranchi. U. 1979.* Ans. $CHCl_3$.

CHAPTER 6

Problems on equivalent weights and atomic weights :

Equivalent weight of a substance (element) is the parts by weight of the substance which can either combine with or displace 1·008 part by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine.

Equivalent weight of a compound : It is that weight of a compound either which contains equivalent weight of an active element or with which it can combine with the equivalent weight of an element or another compound. The equivalent weight of any compound can be calculated from the reaction expressing its action on any substance whose equivalent weight is already known.

Example : Calculation of equivalent weight of Na_2CO_3 (anhydrous). We know $Na_2CO_3 + H_2SO_4 = \downarrow Na_2SO_4 + \downarrow H_2O + \uparrow CO_2$

106 gm 98 gm

98 gms of $H_2SO_4 \equiv 106$ gms of Na_2CO_3.

Or, 49 gms of $H_2SO_4 \equiv 53$ gms of Na_2CO_3.

Hence, the equivalent weight of $Na_2CO_3 = 53$. ∵ equivalent weight of $H_2SO_4 = 49$.

Equivalent weight of an acid :

$$\text{Equivalent weight of an acid} = \frac{\text{Molecular weight of the acid}}{\text{Number of replaceable hydrogen atoms present per molecule}} = \frac{\text{Molecular weight}}{\text{Basicity}}.$$

Example : equivalent weight of sulphuric acid $= \frac{2+32+64}{2} = 49.$

Equivalent weight of an alkali :

$$\text{Equivalent weight of an alkali} = \frac{\text{Molecular weight of the alkali}}{\text{Acidity}}.$$

Example : equivalent weight of $NaOH = \frac{23+16+1}{1} = 40.$

Equivalent weight of a salt :

$$\text{Equivalent weight of a salt} = \frac{\text{Molecular weight of the salt}}{\text{Total number of valencies of the cations (positive charged particles) present in a molecule of the salt or number of electrons changed in the reaction.}}$$

Example : Calculate the equivalent weight of $KBrO_3$ & $Na_2S_2O_3,\ 5H_2O$ on the following reactions : [S=32·1]

(i) $2S_2O_3^{--} + I_2 = S_4O_6^{--} + 2I^-$

(ii) $BrO_3^- + 6H^+ + 6e^- = Br^- + 3H_2O$. *I. I. T.* 1979.

$$\text{Eq. wt of } KBrO_3 = \frac{39{\cdot}1 + 79{\cdot}9 + 48}{6} = 27{\cdot}83\ ;$$

$$\text{eq. wt of } Na_2S_2O_3.\ 5H_2O = \frac{248{\cdot}2}{1} = 248{\cdot}2.$$

Example : The equivalent weight of $Al_2(SO_4)_3$

$$= \frac{27 \times 2 + (32 + 64) \times 3}{3 \times 2} = 57.$$

W. B. H. S. C (Vocational) 1978.

$\because$ total number of valencies of the cations = 6.

Equivalent weight of a radical : It is that weight of a radical with which it can exist in combination with equivalent weight of an element.

Example : In ammonium chloride (NH_4Cl) the radical (NH_4) exists in combination with the element chlorine.

In this compound 18 parts by weight of NH_4 exist in combination with 35·5 parts by weight of chlorine.

$\therefore$ the equivalent weight of the radical (NH_4) = 18.

$\because$ equivalent weight of chlorine = 35·5.

N.B. Gram eqaivalent weight is the equivalent weight, expressed in gram. 1 gm equivalent weight of a substance either combines with or displaces 1·008 gm of hydrogen (11200cc at S.T.P.) or 8 gms of oxygen (5600cc at S.T.P.) or 35·5 gms of chlorine (11200 cc at S.T.P.)

Equivalent weight can be determined by following methods :

(1) *Oxide method* : equivalent weight

$$\text{of a substance (element)} = \frac{\text{weight of the substance} \times 8}{\text{weight of oxygen}}$$

(2) *Chloride method*: equivalent weight

$$\text{of a substance (element)} = \frac{\text{weight of the substance} \times 35{\cdot}5}{\text{weight of chlorine}}$$

(3) *Hydrogen displacement method*:

$$\text{Equivalent wt. of a substance (element)} = \frac{\text{weight of the substance} \times 1{\cdot}008}{\text{weight of hydrogen displaced}}$$

$$= \frac{\text{weight of the substance} \times 1{\cdot}008}{\text{Volume of hydrogen at S T.P.} \times 0\ 00009}$$

∵ 1cc hydrogen at S.T.P = 0·00009 gm ;
equivalent weight of hydrogen = 1·008.

(4) *Valency and atomic weight*:

$$\text{equivalent weight} = \frac{\text{atomic wt.}}{\text{valency}}$$

(5) Displacement method :
$$\frac{\text{weight of a substance X}}{\text{weight of another substance Y}} = \frac{\text{eq. wt of X}}{\text{eq. wt of Y}}$$

Or,
$$\frac{\text{weight of a metal } M_1}{\text{weight of another metal } M_2} = \frac{\text{eq. wt of metal } M_1}{\text{eq. wt of metal } M_2}.$$

Atomic weight: Taking hydrogen as standard, atomic weight

$$\text{of an element} = \frac{\text{weight of one atom of element}}{\text{weight of one atom of hydrogen}}.$$

It is a number (dimensionless quantity) which shows how many times one atom of an element is heavier than one atom of hydrogen. 1 gram atomic weight is the atomic weight, expressed in gram. [Carbon, Oxygen may be taken as standard]

Atomic weight can be determined by following methods :

(1) **Cannizzaro's method:** This method based on the fact that atoms are indivisible. Therefore the molecule of a compound can not contain less than one atom of a particular element. Consequently the smallest weight of an element present in the molecular weights of a large number of its compounds may represent the atomic weight of the element. If this least weight of the element present in the different molecular weights of its compounds be determind, it may probably correspond to the atomic weight of the element.

Numerical Example :

The following results were obtained by analysis of 4 gaseous compounds of the element :

Compound→	A	B	C	D
Vapour density→	22	13	15	39
Percentage of element in the compd→	27·3	92·3	80·0	92·3

Determine the atomic weight of the element from the data.

Patna University ; *Bhagalpur*. U. 1963.

Compd	Density	Mol. wt	°/₀ of the element	wt of the element in the mol. wt.
A	22	$22\times2=44$	27·3	$\frac{27{\cdot}3\times44}{100}\approx12$
B	13	$13\times2=26$	92·3	$\frac{92{\cdot}3\times26}{100}\approx2\times12$
C	15	$15\times2=30$	80·0	$\frac{80\times30}{100}\approx2\times12$
D	39	$39\times2=78$	92·3	$\frac{92{\cdot}3\times78}{100}\approx6\times12$

$\because$ molecular weight $= 2\times$ vap. density.

The smallest weight of the element in the different molecular weights of the compounds is 12 which is therefore the atomic weight of the element.

(2) **Isomorphism method :**

Isomorphous compounds contain the same number of atoms combined in a similar fashion.

Example : For a pair of isomorphous compounds e.g ;

$$\text{ABC and ADC, } \frac{\text{atomic wt of B}}{\text{atomic wt of D}}$$

$$=\frac{\text{wt of B combining with fixed wt of A and C}}{\text{wt of D combining with fixed wt of A and C}}$$

(3) Dulong and Petits' law method :

Atomic weight $\times$ specific heat $\approx 6{\cdot}4$ cals.

$$\therefore \text{ rough atomic weight} = \frac{6{\cdot}4}{\text{specific heat}}.$$

$\because$ specific heat is expressed in calories

$\therefore$ atomic weight $= \frac{[\text{Cals}]}{[\text{Cals}]} =$ a number (a dimensionless quantity).

Specific heat is defined as the amount of heat required to raise the temperature of 1 gm substance through 1°C.

N. B. Value of atomic wt may be either integer or fraction. Fractional atomic weights are found because of the presence of isotopes in the subtance. In such cases mean of atomic weights is calculated from the relative abundance of the substance (element).

Solved problems :

1. If a solid element burns in oxygen without any change in volume (of gas) under the same conditions of temperature and pressure, and if the pure gaseous product has a density of 32, what is the equivalent weight of the element ?

I. I. T. (Group A) 1968.

Since the solid element burns in oxygen without any change in volume under the same conditions of temperature and pressure, 1 volume of its gaseous product formed contains 1 volume of oxygen.

or, 1 molecule of its gaseous oxide contains 1 molecule of oxygen by Avogadro's hypothesis.

So, the molecular weight of the gaseous oxide = weight of the element + weight of 1 molecule of oxygen.

or, $2 \times 32 =$ weight of the element $+ 32$ $\because$ Mol. wt $= 2 \times$ vap. density.

$\therefore$ weight of the element $= 64 - 32 = 32$. $\because$ Wt. of $O_2 = 16 \times 2 = 32$.

Now, 32 parts by weight of oxygen combine with 32 parts by weight of the element.

$\therefore$ 8 parts by weight of oxygen combine with $\frac{32 \times 8}{32} = 8$ parts by weight of element.

The equivalent weight of the element is therefore 8.

2. 0·1827 gm of a chloride of an element contains 0·1079 gm of chlorine. Calculate the equivalent weight of the element.

Orissa. Pre. U. 1968.

0·1079 gm of chlorine combines with (0·1827 − 0·1079) gm of an element.

$\therefore$ 35·5 gms of chlorine combine with $\dfrac{0{\cdot}0748 \times 35{\cdot}5}{0{\cdot}1079}$ $= 24{\cdot}609$ gms of the element. Equivalent weight of the element is therefore 24·609.

3. 0·218 gm of a metal on reaction with sulphuric acid gives 218·2 ml of hydrogen at 17°C and 754 mm pressure. Calculate equivalent weight of the metal. [Aqueous tension at 17°C= 14 mm]

Nagpur Pre. U. 1971 ; *Bihar. H. S.* 1964. *Supp.*

We have, $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$ or, $\dfrac{760 \times V_1}{273} = \dfrac{754 \times 218{\cdot}2}{273 + 17}$

$$\text{or,} \quad V_1 = \frac{754 \times 218{\cdot}2 \times 273}{290 \times 760} = 203{\cdot}787 \text{ ml} = \text{volume}$$

of hydrogen liberated at S. T. P.

$\because$ 1 ml hydrogen at S. T. P. = 0·00009 gm.

$\therefore$ 203·787 ml hydrogen at S. T. P. = 0·00009 × 203·787 gm = 0·0183 gm.

0·0183 gm hydrogen is liberated, on reacting 0·218 gm metal with sulphuric acid.

$\therefore$ 1·008 gm hydrogen is liberated, reacting $\dfrac{0{\cdot}218 \times 1{\cdot}008}{0{\cdot}0183}$ gm. metal with sulphuric acid.

$\because$ equivalent weight of hydrogen = 1·008.

$\therefore$ equivalent weight of the metal $= \dfrac{0{\cdot}218 \times 1{\cdot}008}{0{\cdot}0183} = 11{\cdot}967$

$\approx 12.$

4. Cuprous sulphide and silver sulphide are isomorphous compounds. The percentage of sulphur in the former is 20·14 and in the latter is 12·94. The atomic weight of copper is 63·57. Calculate the atomic weight of silver.

In Cu_2S, 100 − 20·14 = 79·86 gms of Cu combine with

20·14 gms of sulphur. In Ag_2S, $100-12{\cdot}94=87{\cdot}06$ gms of Ag combine with 12·94 gms of sulphur.

or, 20·14 gms of sulphur combine with $\dfrac{87{\cdot}06\times20{\cdot}14}{12{\cdot}96}$

$=135{\cdot}5$ gms of Ag.

We have, according to law of isomorphism,

$$\frac{\text{atomic wt of silver}}{\text{atomic wt of copper}}=\frac{135{\cdot}5}{79{\cdot}86}$$

$$\text{or,}\quad \frac{\text{atomic wt of silver}}{63{\cdot}57}=\frac{135{\cdot}5}{79{\cdot}86}$$

$$\therefore\ \text{atomic wt of silver}=\frac{135{\cdot}5\times63{\cdot}57}{79{\cdot}86}=107{\cdot}9.$$

5. Potassium perrhenate is isomorphous with potassium permanganate ($KMnO_4$) and it contains 64·37 percent of rhenium. Calculate the atomic wt of rhenium.

Since the molecular formula of potassium perrhenate is the same as that of $KMnO_4$.

∴ molecular weight of potassium perrhenate

$=39+X+16\times4.$

Where, X=at. wt of rhenium ; at. wt of K=39 ; at. wt of oxygen=16.

or, $(39+X+64)$ gms of potassim perrhenate contain X gm of rhenium. ∴ the percentage of rhenium in the potassium perrhenate$=\dfrac{X\,.\,100}{39+X+64}$.

By the question, $\dfrac{100X}{39+X+64}=64{\cdot}37.$ ∴ $X=186{\cdot}8.$

6. A sample of metal oxide weighing 6·5 gms is decomposed quantitatively to give 6·251 gms of the metal. The specific heat of the metal is 0·0332. Calculate the exact atomic weight of the metal. *I. I. T. Adn. T.* 1969.

0·249 gm oxygen combined with 6·251 gms of the metal in the metal oxide.

∴ 8 gms of oxygen „ „ $\dfrac{6{\cdot}251\times8}{0{\cdot}249}=200{\cdot}80$ gms „ „ „ .

Equivalent weight of the metal is therefore 200·80.

Again, according to Dulong—Petits' law,

$$\text{rough atomic weight} = \frac{6.4}{\text{specific heat}} = \frac{6.4}{0.0332} = 192.77.$$

$$\text{Now, eq. wt} = \frac{\text{at. wt}}{\text{valency}} \quad \text{or, valency} = \frac{192.77}{200.80} = 0.96.$$

Since valency must be an integer, exact valency of the metal is therefore 1.

$\therefore$ exact atomic wt of the metal = eq. wt. × valency

$= 200.80 \times 1 = 200.80.$

7. Naturally occurring boron consists of two isotopes whose atomic weights are 10·01 and 11·01. The atomic weight of natural boron is 10·81. Calculate the percentage of each isotope in natural boron. *I. I. T. (Group A). 1978.*

Let X be the number of atoms of one of the two isotopes.

$\therefore$ '100 -- X' is the number of atoms of the another isotope.

Now, wt of one of the two isotopes + wt of the another isotope

= total wt of the naturally occurring boron.

or, $X.10.01 + (100 - X).\,11.01 = 10.81.100.$ $\therefore$ $X = 20.$

Percentage of one of the two boron isotopes = 20.

Percentage of the another isotope = 80.

8. 1.2 gms of sodium chloride was dissolved in water and the solution treated with excess of silver nitrate. The weight of the precipitated silver chloride after washing and drying was found to be 2·94 gms. Calculate the equivalent weight of sodium. (At. wt of Ag = 108) Punjab P.U. 1969.

$$\text{We have, } \frac{\text{wt of sodium chloride}}{\text{wt of silver chloride}} = \frac{\text{eq. wt of sodium choride}}{\text{eq. wt of silver chloride}}$$

$$\text{or, } \frac{1.2}{2.94} = \frac{\text{eq. wt of Na} + \text{eq. wt of Cl}}{\text{eq. wt of Ag} + \text{eq. wt of Cl}} = \frac{\text{eq. wt of Na} + 35.5}{108 + 35.5}$$

$\therefore$ eq. wt of Na = 23·071.

Miscellaneous

9. 1·878 gms of a metal bromide MBr_x when heated in a stream of hydrogen chloride gas is completely converted to the chloride MCl which weighs 1·000 gm. The metal M has a specific heat of 0·14 cal/g/°C. Calculate the molecular weight of the metal bromide. I. I. T. (GpB) 1968.

(A) **Calculation of the equivalent weight of metal (M) :**

$$\frac{\text{wt of MBr}_x}{\text{wt of MCl}_x}=\frac{\text{eq.wt of MBr}_x}{\text{eq.wt of MCl}}\text{Or, }\frac{1{\cdot}878}{1{\cdot}000}=\frac{\text{eq.wt of M}+80}{\text{eq.wt of M}+35{\cdot}5}$$

∴ eq. wt of M = 15·18.

(B) **Calculation of the atomic weight of the metal. (M) :**

(i) Approximate atomic weight calculation :

$$\text{Approximate atomic weight}=\frac{6{\cdot}4}{0{\cdot}14}=45{\cdot}7.$$

(ii) **Calculation of valency of the metal (M) :**

$$\text{Valency}=\frac{\text{at.wt}}{\text{eq.wt}}=\frac{45{\cdot}7}{15{\cdot}18}\approx 3.$$

(iii) **Calculation of correct atomic weight of the metal :**

At. wt = eq. wt × valency = 15·18 × 3 = 45·54.

(C) **Calculation of the mol. wt of MBr_x :**

Here, $x=3$. The formula of metal bromide is therefore MBr_3. ∴ mol. wt of metal bromide

= at.wt of M + 3. at.wt of Br = 45·54 + 3·80 = 285·54.

10. On dissolving 2 gms of a metal in sulphuric acid, 4·51 gms of the metal sulphate was formed. The specific heat of the metal is 0·057 cal/g/°C. What is the valency of the metal and its exact atomic weight ? *I.I.T.* (Gp. A) 1978.

$$\frac{\text{wt of metal}}{\text{wt of metal sulphate}}=\frac{\text{eq.wt of metal}}{\text{eq.wt of metal}+\text{eq.wt of sulphate}}$$

$$\text{Or, }\frac{2}{4{\cdot}51}=\frac{\text{eq.wt of metal}}{\text{eq.wt of metal}+48}\therefore\ \text{eq.wt of metal}=38{\cdot}247.$$

$$\text{Approximate at.wt}=\frac{6{\cdot}4}{0{\cdot}057}=112{\cdot}28.$$

$$\text{Valency}=\frac{\text{at.wt}}{\text{eq.wt}}=\frac{112{\cdot}28}{38{\cdot}247}$$

= 2·935 ≈ 3. ∴ correct at. wt of the metal = eq.wt × valency = 38·247 × 3 = 114·741.

11. It was observed that 10 gms of silver combine with 6·1 gms of metal chloride whose vapour density is 7·0 (air = 1). Find the exact atomic weight of the metal. (Ag = 108, Cl = 35·5, vapour density of air = 14·48)

108 gms of silver combine with 35·5 gms of chlorine.

$\therefore$ 10 gms of silver combine with $\frac{35{\cdot}5\times10}{108}$

$=3{\cdot}288$ gms of chlorine.

Again, wt of metal = wt of metal chloride—wt of chlorine.

$\therefore$ wt of metal $=6{\cdot}1-3{\cdot}288=2{\cdot}812$ gms.

Equivalent wt of the metal $=\frac{2{\cdot}812\times35{\cdot}5}{3{\cdot}288}=30{\cdot}36.$

'X' is supposed to be the valency of the metal. The molecular formula of the metal chloride is therefore MCl_x. Mol. Wt of $MCl_x=2.$ vapour density of MCl_x (H=1). Vapour density of MCl_x (H=1) = vapour density of MCl_x (air=1).

vapour density of air $=7\times14{\cdot}48=101{\cdot}36.$

Mol. wt of metal chloride $(MCl_x)=2\times101{\cdot}36=202{\cdot}72.$

Now, mol. wt of metal chloride = at. wt of M + at. wt of chlorine. X or $202{\cdot}72=$ eq.wt of M. valency $+35\ 5$ X.

or, $202{\cdot}72=30{\cdot}36X+35{\cdot}5X\quad\therefore\quad X=3{\cdot}07\approx3.$

Exact atomic weight of the metal $(M)=30{\cdot}36\times3=91{\cdot}08.$

12. The specific heat of an element varies with temperature but obtained a value of 0·054 at 30°C. The element forms two oxides *A* and B. One gm of each of these two oxides when heated on charcoal gives respectively 0·2263 and 0·2851 gm of carbon dioxide. Calculate atomic weight of the element and write down the simplest formulae of the two oxides. *Patna University 1969* A.

Approximate at.wt of the element $=\frac{6{\cdot}4}{0{\cdot}054}=118.$

Eq. wt of the element in the oxide A :—

44 gms of CO_2 contain 32 gms of oxygen.

$\therefore$ 1 gm of CO_2 contains $\frac{32}{44}=\frac{8}{11}$ gm of oxygen.

Amount of oxide A = 1 gm ; amount of oxygen removed as CO_2 from the oxide A by carbon $=\frac{8}{11}\times0{\cdot}2263=0{\cdot}1646$ gm.

$\therefore$ amount of element $=1-0{\cdot}1646=0{\cdot}8354$ gm.

Eq. wt of the element in the oxide A $=\frac{0{\cdot}8354\times8}{0{\cdot}1646}=40{\cdot}7.$

Eq. wt of the element in the oxide B :—

Similarly eq.wt of the element in the oxide B = 30·45.

Valency of the element in the oxide $A = \frac{118}{40 \cdot 7} \approx 3$.

Valency of the element in the oxide $B = \frac{118}{30 \cdot 45} \approx 4$.

Exact at.wt of the element in the oxide $A = 40 \cdot 7 \times 3 = 122 \cdot 1$.

Exact at.wt of the element in the oxide $B = 30 \cdot 45 \times 4 = 121 \cdot 8$.

Formulae of the two oxides A and B are M_2O_3 and M_2O_4 or MO_2 respectively.

13. The equivalent weight of a metal M is 29·4. What will be the volume of hydrogen at 10°C and 750 mm. pressure, if 0·444 gm of the metal reacts with dilute sulphuric acid ? *Ranchi University. Supp. 1968.*

29·4 gms of the metal (M) liberate 1·008 gm of hydrogen

∴ 0·444 gm „ „ „ liberates $\frac{1 \cdot 008 \times 0 \cdot 444}{29 \cdot 4} = 0 \cdot 015$ gm. „ „.

We have, $PV = \frac{W}{M} RT$ or, $\frac{750 \times V}{760}$

$$= \frac{0 \cdot 015 \times 0 \cdot 0821 \times (273+10)}{2}$$

∴ V = 0·176 litre = 176cc. The volume of hydrogen at 10°C and 750 mm pressure is therefore 176 cc.

[We have, $PV = \frac{W}{M} RT$; $\frac{760 \times V}{760} = \frac{0 \cdot 015}{2} \times 0 \cdot 0821 \times 273$.

Or, V = 0·168 litre at N.T.P.

Again, $\frac{PV}{T} = \frac{P_1 V_1}{T_1}$; $\frac{1 \times 0 \cdot 168}{273} = \frac{V_1 \times \frac{750}{760}}{283}$

∴ $V_1 = 0 \cdot 176$ litre = 176cc at 750 mm pressure and 10°C temp.]

14. *A* metal on being heated in a current of chlorine yields a liquid containing 54·4% chlorine. 0.522 gm of this compound gave 47·6cc of vapour at 15°C and 754 mm pressure. Find its molecular formula. [Cl = 35·46] *Ranchi*. U. 1971.

54·4 parts by wt of chlorine combine with $(100-54{\cdot}4)=45{\cdot}6$ parts by wt of the metal.

$\therefore$ 35·46 parts by wt of chlorine combine with $\frac{45{\cdot}6\times35{\cdot}46}{54{\cdot}4}$ $=29{\cdot}723$ parts by wt of the metal.

$\therefore$ eq.wt of the metal $=29{\cdot}723$.

We have, $PV=\frac{W}{M}RT$; $\frac{754\times47{\cdot}6}{760\times1000}$

$$=\frac{0{\cdot}522\times0{\cdot}0821\times(273+15)}{M}$$

$\therefore$ $M=261{\cdot}361$. Mol. Wt of the metal chloride (liquid) is therefore 261·361. Let X be the valency of the metal. Formula of the metal chloride therefore MCl_x. Again, mol. wt of metal chloride = at. wt of M + at. wt of chlorine. valency.

or, $261{\cdot}361=$ at. wt of $M+35{\cdot}460X$

$=$ eq. wt of M. valency $+35{\cdot}460X$.

or, $261{\cdot}361=29{\cdot}723X+35{\cdot}460X=65{\cdot}183X$

$$\therefore\ X=\frac{261{\cdot}361}{65{\cdot}183}=4.$$

Molecular formula of the compound is therefore MCl_4.

15. A piece of metal weighs between 0·5 and 0·6 gm. When it dissolves in dilute acid, 196 cc of H_2 measured at N. T. P. are evolved. If the correct at. wt of the metal be 65·2, calculate the exact weight of the piece of metal dissolved in the acid (one litre of H_2 at N. T. P. weighs 0·09 gm); *Bhagalpur.* U. *1973, 1976*; *Patna.* U. *1973 A*; *Ranchi.* U. *1968A, '73S*; *M.* U. *1967S, 1976A*; *L. N.* M. U. *'74A*; *Bombay '67.*

Let w be the weight of metal in gm.

$\because$ 1000 cc of H_2 at N. T. P. weigh 0·09 gm.

$\therefore$ 196 cc of H_2 at N. T. P. weigh $\frac{0{\cdot}09\times196}{1000}=0{\cdot}0176$ gm.

0·0176 gm of H_2 is evolved, when w gm metal dissolves in acid.

$\therefore$ 1·008 gm of H_2 is evolved, when $\frac{w\times1{\cdot}008}{0{\cdot}0176}$ gm metal dissolves in

Equivalent weight of the metal $= \dfrac{w \times 1{\cdot}008}{0{\cdot}0176}$

$\because$ eq. wt of $H_2 = 1{\cdot}008$.

Again, equivalent weight $= \dfrac{\text{at. wt}}{\text{valency}}$ or $\dfrac{w \times 1{\cdot}008}{0{\cdot}0176} = \dfrac{65{\cdot}2}{\text{valency}}$

or, $w = \dfrac{65{\cdot}2 \times 0{\cdot}0176}{1{\cdot}008 \times \text{valency}}$.

When, valency $= 1$; $w = \dfrac{65{\cdot}2 \times 0{\cdot}0176}{1{\cdot}008 \times 1} = 1{\cdot}138$ gm.

When, valency $= 2$; $w = \dfrac{1{\cdot}138}{2} = 0{\cdot}569$ gm.

When, valency $= 3$; $w = \dfrac{1{\cdot}138}{3} = 0{\cdot}379$ gm.

As the metal weighs between 0·5 and 0·6 gm, the weight corresponds to valency $= 2$ is the exact weight of the piece of the metal, dissolved in the acid.

16. A metal M which in divalent is its ordinary salts, forms an oxide which contains 90·66% of the metal. When 13·70 gms of its oxide were treated with nitric acid, 13·24 gms of the nitrate were formed, and an insoluble residue weighing 4·78 gms was left. The residue was shown by analysis to be another oxide of M containing 86·61% of M. From these data calculate the formulae of two oxides and the atomic weight of M.

$$\frac{\text{weight of oxide}}{\text{weight of nitrate}} = \frac{\text{equivalent weight of metal} + \text{eq. wt of oxygen}}{\text{equivalent weight of metal} + \text{eq. wt of nitrate}}$$

or, $\dfrac{8{\cdot}92}{13{\cdot}24} = \dfrac{z+8}{z+62}$ $\because$ $13{\cdot}70 - 4{\cdot}78 = 8{\cdot}92 =$ amount of metal oxide in which metal is divalent, reacted with nitric acid.

Here, eq. wt of metal $= z$; eq. wt of oxygen $= 8$; eq. wt of nitrate $= 62$. $\therefore$ $z = 103{\cdot}50$. At. wt of the metal $= 103{\cdot}50 \times 2 = 207{\cdot}00$. Now, number of atoms of M : number of atoms of oxygen $= \dfrac{90{\cdot}66}{207} : \dfrac{9{\cdot}34}{16} = 0.438 : 0{\cdot}584 = 1 : \dfrac{0{\cdot}584}{0{\cdot}438} = 1 : 1{\cdot}33 = 3 : 4$.

Formula of this metal oxide in which metal is 90·66% in amount, therefore M_3O_4.

Formula of another metal oxide in which metal is 86·61% in amount :

Number of atoms of M : number of atoms of oxygen

$=\frac{86\cdot61}{207}:\frac{13\cdot39}{16}=0\cdot418:0\cdot837=1:\frac{0\cdot837}{0\cdot418}=1:2.$ Formula of the metal oxide is therefore MO_2.

17. A metal forms two oxides. The higher oxide contains 20% oxygen while 4·29 gms of the lower oxide when converted into higher weigh 4·77 gms. Find the two equivalent weights of the metal.

The higher oxide contains 20% oxygen.

or 80 gms of the metal combine with 20 gms of oxygen.

$\therefore$ equivalent weight of the metal in higher oxide $=\frac{80\times8}{20}=32.$

Again, 4·29 gms of lower oxide combine with (4·77 − 4·29) gms of oxygen to form the higher oxide.

$\therefore$ equivalent weight of the lower oxide $=\frac{4\cdot29\times8}{4\cdot77-4\cdot29}$

$$=\frac{4\cdot29\times8}{0\cdot48}=70.$$

Now, one gm. equivalent weight of the lower oxide should contain 8 gms of oxygen. $\therefore$ equivalent weight of the metal in lower oxide $=70-8=62.$

18. 1·307 gm of the hydrated chloride of a metal M was heated to a constant weight, the final weight of the anhydrous chloride being 1·114 gm. Treated with an excess of sulphuric acid, 1·582 gm of the anhydrous chloride gave 1·774 gm of the anhydrous sulphate. The specific heat of the metal is 0·047. Calculate the accurate atomic weight of the metal and write the formula for its hydrated chloride. (Cl = 35·5 ; S = 32 ; H = 1 ; O = 16). *Panjab. U. I. Sc. 1961 ; Kashmir 1973.*

We have, $\frac{\text{wt of anhydrous chloride}}{\text{wt of anhydrous sulphate}}=\frac{\text{eq. wt of metal}+35\cdot5}{\text{eq. wt of metal}+48}$

$\therefore$ eq. wt of metal $=67\cdot49$. $\because$ eq. wt of $SO''_4=\frac{98}{2}=48.$

Approx. at wt $=\frac{6\cdot4}{0\cdot047}=136\cdot17$; valency $=\frac{136\cdot17}{64\cdot49}\approx2.$

Exact at. wt $=67{\cdot}49\times2=134{\cdot}98$; formula of anhydrous chloride is MCl_2, where M stands for metal. Mol. Wt of anhydrouschloride $=134{\cdot}98+71{\cdot}00=205{\cdot}98$. Now, 1·114 gm anhydrous metallic chloride is obtained from 1·307 gm hydrated metallic chloride. So, water present in the metallic chloride $=1{\cdot}307-1{\cdot}114=0{\cdot}193$ gm wt of water combined with mol. wt of anhydrous chloride $=\dfrac{0{\cdot}193\times205{\cdot}98}{1{\cdot}114}=35{\cdot}70$. ∴ number of water moles $=\dfrac{35{\cdot}7}{18}\approx2$.

Formula of the hydrated metallic chloride is therefore MCl_2, $2H_2O$.

19. 4·215 g of a metallic carbonate was heated in a hard glass tube and the CO_2 evolved was found to measure 1336 ml at 27°C and 700 mm pressure. What is the equivalent weight of the metal ? *I. I. T. 1979.*

$$\frac{PV}{T}=\frac{P_0V_0}{T_0} \quad \text{or} \quad \frac{700\times1336}{237+27}=\frac{760\times V_0}{273}$$

$$\text{or,}\quad V_0=1119{\cdot}77 \text{ cc.}$$

22400 cc CO_2 weigh 44 gms. ∵ mol. wt of $CO_2=44$.

1119·77 „ „ „ $\dfrac{44\times1119{\cdot}77}{22400}=0{\cdot}499$ gm.

Wt of metallic carbonate $=4{\cdot}215$ gms.
Wt of carbon dioxide $=0{\cdot}499$ gm.
∴ wt of metallic oxide $=3{\cdot}716$ gms.

$$\frac{\text{Wt of metallic carbonate}}{\text{Wt of metallic oxide}}=\frac{\text{eq. wt of metal}+\text{eq. wt of carbonate}}{\text{eq. wt of metal}+\text{eq. wt of oxygen}}$$

$$\text{or}\quad \frac{4{\cdot}215}{3{\cdot}716}=\frac{M+30}{M+8} \quad \therefore\ M=\text{eq. wt. of metal}=155{\cdot}83.$$

20. Calculate the number of oxygen atoms in 6·92 gms of orthophosphoric acid. (H—1, P—31, O—16).

1 gm mole orthophosphoric acid $=98$ gms.

∵ formula of orthophosphoric acid is H_3PO_4.

or, 98 gms of orthophosphoric acid contain
$6{\cdot}023\times10^{23}$ number of molecules.

$\therefore$ 6·92 gms of orthophosphoric acid contain
$\frac{6{\cdot}023\times10^{23}\times6{\cdot}92}{98}$ „ „ „

Again, 1 molecule of orthophosphoric acid contains
4 atoms of oxygen.

$\therefore$ $\frac{6{\cdot}023\times10^{23}\times6{\cdot}92}{98}$ molecules „ „ „
$\frac{4\times6{\cdot}023\times10^{23}\times6{\cdot}92}{98}$ atoms of oxygen

$\therefore$ number of oxygen atoms in 6·92 gms of orthophosphoric acid $=\frac{4\times6{\cdot}023\times10^{23}\times6{\cdot}92}{98}=1{\cdot}7\times10^{23}$.

21. A compound was found to contain 5·37 percent nitrogen. What is the minimum molecular weight that could be assigned to the compound ? *I. I. T.* (Gp. B.) *1968.*

One molecule of the compound must possess at least one atom of nitrogen. Hence, the molecular weight of the compound must possess at least 14 parts by wt of nitrogen. If the minimum molecular weight of the compound is supposed to be M, the percentage of nitrogen in it$=\frac{14\times100}{M}$.

Again, the actual percentage of nitrogen$=5{\cdot}37$.

$\therefore$ $\frac{14\times100}{M}=5{\cdot}37$ or $M=260{\cdot}6$.

22. 1 gm of an acid when completely acted upon by Mg gave 1·301 gms of an anhydrous magnesium salt. Find the equivalent weight of acid (Mg=24). *Patna. U. 1973* ; M. U. *1973A.*

We know, equivalent weight of a metal+equivalent weight of acid=equivalent weight of salt+equivalent weight of hydrogen.

or, equivalent weight of acid=equivalent weight of salt +equivalent weight of hydrogen—equivalent weight of metal.

Now, $\frac{\text{equivalent weight of acid}}{\text{equivalent weight of salt}}=\frac{\text{weight of acid}}{\text{weight of salt}}$

or $$\frac{\text{equivalent weight of acid}}{\text{equivalent weight of salt}}=\frac{1}{1{\cdot}301}.$$

∴ equivalent weight of salt $=1{\cdot}301\times$ equivalent weight of acid.

So, equivalent weight of acid $=1{\cdot}301\times$ eqivalent weight of acid + equivalent weight of hydrogen—equivalent weight of metal.

or, equivalent weight of acid $-\,1{\cdot}301\times$ equivalent weight of acid $=1-12=-11.$

∵ eq. wt. of hydrogen $=1$; eq. wt. of Mg $=12.$

or, equivalent weight of acid. $(1-1{\cdot}301)=-11.$

∴ equivalent weight of acid $=\dfrac{11}{0{\cdot}301}=36{\cdot}5.$

Problems for practice

1. The oxide of a bivalent element contains 40% oxygen. Find the atomic weight of the element. *Ranchi.* U. *Pre.* U. *1969.*
Ans. 24

2. A metallic oxide contain 60% of the metal. What is the equivalent weight of the metal ? *West. Bengal. H. S. C. 1978.*
Ans. 12

3. 1·5276 gms of $CdCl_2$ was found to contain 0·9367 gm of cadmium. Calculate the atomic weight of cadmium.
I. I. T. (Gp. A) 1975. Ans. 112·52.

4. 164 milligram of a metal when dissolved in HCl evolves 31 cc. of hydrogen at N. T. P. Calculate the equivalent weight of the metal. *West. Bengal. Adn. T. E. E. 1973.* Ans. 58·78

5. 2·40 gms of calcium on being treated with excess of dilute hydrochloric acid liberate 1344 cc pure hydrogen at N. T. P. Find out the equivalent weight of calcium ? *West. Bengal. H. S. (Tech). 1974.*
Ans. 20

6. What is the equivalent weight of a metal, 24 gms of which evolve from an acid 22·4 litres of hydrogen at N. T. P ? U. *P. Board I. Sc. 1967.*
Ans. 12

7. 1·04 gm of the chloride of a metal on treatment with sulphuric acid gave 1·16 gm of insoluble sulphate of the metal. Calculate the equivalent weight of the metal. *Orissa. P. U. 1968*
Ans. 67·66

8. The oxide of an element contains 25% oxygen. The specific heat of the element is 0·088. Calculate the equivalent weight, valency and atomic weight of the element. *Osmania. Pre.* U. *1968.* Ans. 72

9. 0·5 gm of a metal on oxidation gave 0·63 gm of oxide. Its specific heat was found to be 0·1. Calculate its atomic weight. *Kurukshetra. P. U. 1968.* Ans. 62·4

10. The specific heat of a metal is 0·237. On analysis its chloride gave 79·77% chlorine. Determine its atomic weight and valency. *All India H. S. 1968.* Ans. 27·13

11. What is the valency of an element of which the equivlent weight is 12 and the specific heat is 0·25 ? *I. I. T. (Gp. B) 1971.* Ans. 2

12. If the vapour density of the chloride of an element M is 66·75 and the oxide of the element contains 53% of the element, calculate the valency and the atomic weight of the element. *West. Bengal. Adn. T. E. E. 1970.* Ans. 3 ; 27

13. The vapour density of the chloride of a metal is 66 and the oxide of the metal contains 53% of the metal. Calculate valency and atomic weight of the metal. (Cl = 35·5). *Bhagalpur.* U. *'74 ; Ranchi.* U. *Pre.* U. *Supp. 1970.* Ans. 3 ; 27.

14. The specific heat of the metal is 0·152. 0·0564 gm of the oxide of the metal yielded 0·2014 gm of the anhydrous bromide. Calculate the at. wt of the metal. (O = 16 ; Br = 80) *Ranchi.* U. *1975A.* Ans. 40

15. 2·380 gms of a metal on treatment with nitric acid and subsequent ignition gave 3·022 gms of the oxide. Specific heat of the metal is 0·055. Calculate the exact atomic weight of the metal. *Ranchi.* U. *1974.* Ans. 118·92

16. A sample of a metal chloride weighing 0·22 gm required 0·51 gm of silver nitrate to precipitate the chloride completely. The specific heat of the metal is 0·057. Find the molecular

formula of the chloride if the symbol of the metal is M. [At. wt : N=14 ; O=16 ; Cl=35·5 ; Ag=107·9]. *W. B. H. S. 1976 ; I. I. T. (Gp. B) 1976.* Ans. MCl_3

[Hints : eq. wt of $AgNO_3$ reacts with eq. wt of metal chloride. From this find out eq. wt. of metal chloride. Subtract eq. wt of chloride from eq. wt of metal chloride to get eq. wt of metal.]

17. Two oxides of a metal containing 36·8% and 30·38% of oxygen. The specific heat of the metal is 0·117. Assign the formula of the two oxides (Valency of oxygen=2). *Patna University.* Ans. M_2O_4 ; M_2O_3

18. Calculate the number of phosphorous atoms when there is 0·519 mole of phosphorous (P_4). Ans. $1·25 \times 10^{24}$

19. The equivalent weight of the metal is 40. What is volume of oxygen that would combine with 0·31 gm of the metal at 15°C and 720 mm pressure ? Vap. pre. at 15°C=12·8 mm. Ans. 49·20 cc

20. The equivalent weight of a metal is 36. What weight of the metal would give 9·322 gms of its chloride ? Ans. 4·693 gms.

21. The equivalent weights of two metals M_1 and M_2 are respectively 24 and 42. What weight of M_1 would get displaced from its salt solution by 2·1 gms of the metal M_2 ? Ans. 1·2 gms

22. 2·47 gms of CuO were obtained by oxidising 1·986 gms of copper by nitric acid. 0·335 gm of Cu was precipitated by 0·346 gm of Zn from $CuSO_4$ soln. What are the eq. wts of Cu and Zn. Ans. 32·8 ; 33·7. *Patna University.*

23. 3·7 gms of an oxide of a metal were heated with charcoal. CO_2 produced were absorbed in caustic soda and weighed 1 gm. Find the equivalent wt of the metal. Ans. 32·8. *Patna University.*

24. A metal forms three chlorides containing 23·6%, 38·2% and 48·3% by wt of chlorine respectively. The vapour densities

of these chlorides are 74·6, 92·9 and 110·6 respectively. Find the at. wt of the metal and simplest formulae of the compounds.

Ans. MCl ; MCl_2 ; MCl_3.

[Hint. Take help of Cannizzaro's method.]

25. An element A forms chloride which contains 29·34% by wt of chlorine and is isomorphous with potassium chloride. Calculate the at. wt of A. *Calcutta.* U. Ans. 85·5

26. Potassium selenate is isomorphous with potassium sulphate and contains 35·75% of selenium. Find out the at. wt of selenium. *All India H. S. 1969.* Ans. 79

27. Crystalline zinc sulphate is isomorphous with magnesium sulphate ($MgSO_4$, $7H_2O$) and is found to contain 22·6% zinc. Calculate the at. wt of zinc (Mg = 24 ; S = 32). *Bombay University. I. Sc. 1976.* Ans. 64·82

28. A compound M_2O_5 is produced by combination of 8·241 gms of M with 4·09 gms of oxygen. Calculate the at. wt of M. Ans. 80·60

29. Hydrogen has two isotopes with at. wts 1 and 2. If the hydrogen gas has mean at. wt 1·008, find the percentage by weight of each isotope in the hydrogen gas. Ans. 99·2 ; 0·8

30. An element has two isotopes A and B whose at. wts are 69 and 71 respectively. If the percentage by wt of isotope A is 60·2, what is the average at. wt of the element ?

Ans. 69·796

31. In sulphur dioxide there is 50% sulphur. Find out the at. wt of S ? *W. B. H. S. 1977.* Ans. 32

32. The oxide of a metal contains 28·6% oxygen and the vapour density of the chloride of the metal is 55·5. Find out the atomic weight of the metal. M. U. *1970A, '73S* ; *Ranchi.* U. *1977.* Ans. 39 9

33. Calculate the atomic weight of chlorine from the following data and hence find out the number of chlorine atoms in a molecule of chlorine monoxide.

Compounds	Density (air=1)	Percentage composition
Chlorine	2·49	Cl 100
Hydrogen chloride	1·269	Cl 97·23 ; H 2·77
Chlorine monoxide	3·007	Cl 81·58 ; O 18·42
Chlorine peroxide	2·3	Cl 52·55 ; O 47·45

Ans. 35·5, 2

34. One gm of the anhydrous chloride of a metal just reacts with 3·82 gms of silver nitrate ; the vapour density of the chloride is 66·8. What is the at. wt and the valency of the metal ? *Ranchi*. U. *1974*.

Ans. 27·1

35. 1 959 gms of a certain metal when heated in oxygen increases to 2·439 gm. The specific heat of the metal is 0·0944. Find the at. wt. of the metal. *Ranchi*. U. *1973S*. Ans. 65·30

36. A metal M whose sp. heat is 0·11, forms a chloride containing 34·47% of the metal. Calculate (a) its equivalent weight, (b) its atomic weight and (c) the molecular formula of its chloride. *Ranchi*. U. *1967S*. Ans. 18·66 ; 55·98 ; MCl_3.

37. 0·383 gm of the metal when treated with dilute hydrochloric acid displaced 152 cc hydrogen measured over water at 27°C and 746·6 mm pressure. Calculate the equivalent weight of the metal. If the specific heat of the metal be 0·1, what is its exact atomic weight ? (Aqueous tension at 27°C=26·6 mm of mercury. Weight of 1 litre of hydrogen at N. T. P=0.09 gm) *Ranchi*. U. *1968A*.

Ans. 65

38. If the equivalent weight of a metal is 103·5, what weight of the sulphate can be obtained from 10 gms of the chloride ? *Ranchi*. U. *1967A*.

Ans. 10·86 gms

39. The vapour density of a metallic chloride in the vapourous state is 66·8. One gm of the chloride on reaction with excess of silver nitrate gave 3·225 gm of silver chloride. Calculate the at. wt. of the metal. M. U. *1967A*.

Ans. 86

40. What weight of zinc will react with acid to give hydrogen to completely react with oxygen obtained from 30 gms of

potassium chlorate ? [K=39 ; Cl=35·5 ; Zn=65]. *Magadh. U. 1967A* ; *Ranchi.* U. *1973S.* Ans. 47·7

41. The specific heat of metal is 0·27. The chloride of the metal contains 74·7% chlorine. Find out the at. wt. of the metal. *Bhagalpur.* U. *1969A.* Ans. 24

42. On dissolving 0·185 gm of a metal in dilute HCl 71·1 cc of hydrogen gas was collected over water at 18°C and 752·3 mm pressure. Find out the eq. wt of the metal. [Aq. Tension = 15·3 mm at 18°C] *Ranchi.* U. *1970A.* Ans. 31·78

43. The oxide of an element contains 53·3% oxygen. The Vap. Density of the chloride of the element is 85. Find out the valency and at. wt of the element. *Bhagalpur.* U. *1976A.* Ans. 4 ; 9

44. 0·18 gm of a piece of metal on treatment with dil. H_2SO_4, liberates 224 cc of hydrogen at N. T. P. Determine the eq. wt of the metal. *Pat.* U. *'73A.* Ans. 9

45. 0·2332 gm of a chloride of a metal was dissolved in water. This soln ; when treated with excess of $AgNO_3$ soln gave 0·6028 gm of AgCl. The sp. heat of the metal is 0·15. Calculate the eq. wt and at. wt of the element. *Pat.* U. *'73.* Ans. 2, 41·2

46. 1·52 g hydroxide of a metal gives 0·995 g oxide of the metal. Find the eq. wt of the metal. *Patna.* U. *1974A.* Ans. 9·06.

47. When 0·25 gm of a metal reacts with HCl, 223 cc of hydrogen are at N. T. P. If the sp. heat of the metal is 0·254, find out the at. wt of the metal. *R.* U. *'73S.* Ans. 25·1

48. 1·03 gm Zn is shaken with $CuSO_4$ soln, 1 gm Cu separated. Calculate the eq. wt of Cu. (Given, eq. wt of Zn= 32·5) *Magadh.* U. *1975S.* Ans. 31·55

49. 0·1 gm of a metal when dissolved in dil. HCl evolves 124·2 cc of H_2 at N. T. P. The sp. heat of the metal is 0·214. Calculate the at. wt of the metal. *W. B. J. E. E. '77.* Ans. 27·27

50. A molecule of sulphur dioxide contains one atom of sulphur and two atoms of oxygen. The compound contains

50% of sulphur by weight. What is the ratio of atomic weights of sulphur and oxygen ? *W. B. H. S. C. 1979.* Ans. 2

51. The oxide of an element X contains 10·30 percent by weight of oxygen. The specific heat of the element is 0·0305. Calculate the correct atomic weight of the element and write down the formula of the above mentioned oxide. *W. B. J. E. E. 1979.* Ans. 208·98 ; X_2O_3.

52. The oxide of a solid metallic element contains 65·2% of the element. Its atomic weight is 45. What is the valency of the element ? What is the formula of its oxide ? *W. B. H. S. C (Voc) 1979.* Ans. 3 ; M_2O_3

53. Tin completely reacts with sulphuretted hydrogen to form the same volume of hydrogen gas as sulphuretted hydrogen together with tin sulphide. Find out the equivalent weight of sulphur. Vapour density of sulphuretted hydrogen is 17. You are asked not to use formula of any compd.

[Since volume of sulphuretted hydrogen and hydrogen gas is the same, so 1 gm mole sulphuretted hydrogen must give 1 gm mole hydrogen gas under the same conditions of temperature pressure. Again, 1 gm mole of hydrogen = 2 gms ; Vapour density of sulphuretted hydrogen = 17. ∴ Mol. wt of sulphuretted hydrogen = 34. As 2 gm hydrogen come from 34 gm sulphuretted hydrogen, $(34-2)$ gm sulphur is present in 34 gm. sulphuretted hydrogen i.e. 32 gm sulphur combine with 2 gm hydrogen to form 1 gm mole sulphuretted hydrogen. ∴ 1 gm hydrogen must combine with 16 gm sulphur. ∵ equivalent wt of hydrogen = 1 ∴ equivalent wt of sulphur = 32]

54. If *b* gm of silver dissolved in nitric acid, require *a* gm of sodium chloride for complete precipitation as silver chloride, and if *a′* gm of sodium chloride yield *b′* gm of silver chloride, show that the equivalent weight of chlorine is equal to 108. $\left\{\frac{a}{b}\frac{b'}{a'}-1\right\}$. Where 108 is the equivalent weight of silver.

55. 0·18 gm magnesium evolves 182·7 cc of hydrogen from acid at 756·5 mm pressure and 17°C temperature. Hydrogen is collected by displacement of water. Calculate equivalen weight of magnesium. The metal when heated in an environmentt of nitrogen gives a binary compound of magnesium and nitrogen containing 72% magnesium. Calculate equivalent weight of nitrogen. Aqueous tension at 17°C = 14·4 mm] Ans. 4·66

56. 1 g of the chloride of a bivalent metal when treated with an excess of silver nitrate soln, produced 0·965g of silver chloride. Calculate the at. wt of the metal up to two places of decimal assuming the atomic weight of silver = 107·9 and that of chlorine = 35·5. *Calcutta.* U. *B. Sc.* (*A*), *1979.* Ans. 227·30.

57. Calculate the equivalent weight of nitrogen in each of the following conversions. (i) $NO_3 \longrightarrow N_2$ (ii) $N_2 \longrightarrow NH_3$. *I. I. T.* 1979. Ans. 2·33 ; 4·66

CHAPTER 6

Problems on laws of chemical combination

There are five laws of chemical combination. The laws are :

(i) The law of conservation of mass ; (2) the law of constant or definite proportions ; (3) the law of multiple proportions ; (4) the law of reciprocal proportions or equivalent proportions or combining weights and (5) the law of gaseous volumes (Gay Lussac's law).

(1) **The law of conservation of mass** :—The law states that : In a chemical reaction, the total mass (amount) of the reactants equals to the total mass (amount) of the products.

If in a reaction, A and B are the masses of two reactants while C and D are the masses of products formed, then $A+B = C+D$.

Numerical example :

What amount of silver chloride is formed when 1·235 gms. of potassium nitrate, produced by the action of 5·846 gms. of potassium chloride with 3·423 gms. of silver nitrate ? It is assumed that the law of conservation of mass fully holds good.

According to the law of conservation of mass we can write the total mass of the reactants = the total mass of the products *i,e.*, the mass of silver nitrate + the mass of potassium chloride

= the mass of silver chloride + the mass of potassium nitrate.

Let the mass (amount) of silver chloride = $\times$ gms.

$\therefore \quad 3{\cdot}423 + 5{\cdot}846 = \times + 1{\cdot}235, \; \times = 8.034$ gms.

Hence, the amount of silver chloride = 8·034 gms.

(2) **The law of constant or definite proportions (composition)** :—The law states that : A chemical compound always contains the same elements combined together in a constant or definite proportion by weight.

A chemical compound like common salt (sodium chloride) may be obtained from various sources and from various places. It can also be artificially prepared by heating sodium in a jar of chlorine. On analysis, it is found that all samples of pure sodium chloride contain sodium and chlorine only and 23 parts by weight of sodium combine with 35·5 parts by weight of chlorine to produce 58·5 parts by weight of common salt. Thus the ratio of the weights of sodium and chlorine in the compound sodium chloride is always constant.

Numerical examples :

(1) Sodium chloride obtained from three different sources was found to contain sodium and chlorine only and gave the following results : (i) 3·2 gms of sodium chloride contained 1·940 gms. of chlorine ; (ii) 10·0 gm. sodium chloride contained 6·068 gms. of chlorine and (iii) 5·3 gms. of sodium chloride contained 3·216 gms. of chlorine. Show that these are in agreement with the law of constant composition.

(i) 3·2 gms. of sodium chloride contain 1·940 gms. of chlorine

∴ 100 gms. ,, ,, ,, $\frac{1\cdot940}{3\cdot2}\times100=60\cdot62$ gms. ,, ,,

(ii) 10 gms. ,, ,, ,, 6·068 gms. of chlorine.

∴ 100 gms. " ,, ,, $\frac{6\cdot068}{10}\times100=60\cdot68$ gms. ,, ,,

(iii) 5·3 gms. " " " 3·216 gms. of chlorine.

∴ 100 gms. " " ,, $\frac{3\cdot216}{5\cdot3}\times100=60\cdot68$ gms. ,, ,,

The percentages of chlorine in the above three samples of sodium chloride are 60·62, 60·68 and 60·68 respectively and this explains the validity of the law of canstant composition within the limits of experimental error.

(2) Given that (i) 0·36 gm. wt. of a metal when burnt in oxygen yields 0·60 gm. oxide ; (ii) carbonate of that metal contains 28·57% of the metal. Determine, with the help of law of constant proportion, the wt. of the oxide which will be obtained by heating 1 gm. of that carbonate. *West Bengal H. S. 1974.*

0·36 gm metal yields 0·60 gm metal oxide.

∴ 28·57 gm metal yield $\frac{0\cdot60\times28\cdot57}{0\cdot36}=47\cdot616$ gm metal oxide.

So, 100 gm carbonate must yield 47·616 gm metal oxide.

∴ 1 gm carbonate yields $\frac{47\cdot616}{100}=0\cdot47616$ gm metal oxide.

The problem is solved on the basis of law of canstant proportion that the weight ratio of metal and oxygen remains always same in the oxide produced directly from the metal and that of produced on heating carbonate.

The law of multiple proportions : The law states that : when two elements combine to form two or more different compounds, the different weights of one of the elements which combine with a constant weight of the other element, bear a simple ratio to one another.

N. B. (i) Simple ratio means ratio of small whole numbers.

(ii) Small whole numbers are viz. 1, 2, 3, 4 and 5 generally.

If two elements say A and B combine to form three different compounds and let X gms, Y gms and Z gms be the three different weights of one of the elements A that combine with a constant weight *m* gms of B in the three compounds, then according to the law these weights of *A* must bear a simple ratio to one another i.e., X : Y : Z=1 : 2 : 3 or 2 : 3 : 4 or ratio of any other small whole numbers.

Numerical examples :

(1) Carbon combines with hydrogen to form three compounds A, B and C. The percentages of hydrogen in A, B and C are 25 per cent, 14·3 per cent and 7·7 per cent respectively. Which law of chemical combination does this example illustrate ? How ?

I. I. T 1973.

Name of the Compound	Percentage of Hydrogen	Percentage of Carbon
A	25·00	100 − 25 = 75·00
B	14·30	100 − 14·30 = 85·70
C	7·70	100 − 7·70 = 92·30

(a) In compound A, 25 parts by wt of hydrogen combine with 75 parts by wt of carbon.

∴ In compoand A, 1 part by wt of hydrogen combines with $\frac{75}{25}=3$ parts by wt of carbon (app).

(b) In compound B, 14·30 parts by wt of hydrogen combine with 85·70 parts by wt of carbon.

∴ in compound B, 1 part by wt of hydrogen combines with $\frac{85\cdot70}{14\cdot30}=6$ parts by wt of carbon (app).

(c) In compound C, 7·70 parts by wt of hydrogen combine with 92·30 parts by wt of carbon.

∴ in compound C, 1 part by wt of hydrogen combines with $\frac{92 \cdot 30}{7 \cdot 70}=12$ parts by wt of carbon (app).

Thus, the weights of carbon which combine with the same weight of hydrogen are in the ratio 3 : 6 : 12 i.e., 1 : 2 : 4. This is a simple ratio and, hence, the numerical example illustrates the law of multiple proportions.

(2) Two compounds each containing only tin and oxygen had the following compositions :

	wt% of Sn	wt% of O
Compound A	78·77	21·23
Compound B	88·12	11·88

Show how these data illustrate the law of multiple proportions ? *I. I. T.* 1975.

(a) In compound A, 21·23 parts by wt of oxygen combine with 78·77 parts by wt of tin.

∴ in compound A, 1 part by wt of oxygen combines with $\frac{78 \cdot 77}{21 \cdot 23}=3 \cdot 7$ parts by wt of tin.

(b) In compound B, 11·88 parts by wt of oxygen combine with 88·12 parts by wt of tin.

∴ in compound B, 1 part by wt of oxygen combines with $\frac{88 \cdot 12}{11 \cdot 88}=7 \cdot 4$ parts by wt of tin.

Thus, the weights of tin which combine with a fixed weight of oxygen are in the ratio 3·7 : 7·4 i.e., 1 : 2. This is a simple ratio and, hence, the data illustrate the law of multiple proportions.

(4) **The law of reciprocal proportions or equivalent proportions or combining weights :** The law states that : elements combine amongst themselves in the proportion of their equivalent weights or of a simple multiple (or fraction) of them.

Let the equivalent wt of an element A be X gms and that of B be Y gms then according to the above law when A and B combine amongst themselves they will do so in the proportion of their equivalent weights i.e., X : Y or its simple multiple (or fraction).

Numerical examples :

(1) Aluminium oxide contains 52·9% aluminium and carbon dioxide contains 27·27% of carbon. Assuming the law of reciprocal proportions, calculate the percentage of aluminium in aluminium carbide. *All India H. S. 1970.*

In aluminium oxide, 47·1 parts by wt of oxygen combine with 52·9 parts by wt of aluminium.

∴ in aluminium oxide 8 parts by wt of oxygen combine with $\frac{52{\cdot}9\times8}{47{\cdot}1}=8{\cdot}985$ parts by wt of aluminium.

In carbon dioxide, 72·73 parts by wt of oxygen combine with 27·27 parts by wt of carbon.

∴ in carbon dioxide 8 parts by wt of oxygen combine with $\frac{27{\cdot}27\times8}{72{\cdot}73}=2{\cdot}999$ parts by wt of carbon.

Ratio of different weights of aluminium and carbon combined with equivalent weight of oxygen

$$=8{\cdot}985:2{\cdot}999=\frac{8{\cdot}985}{2{\cdot}999}:\frac{2{\cdot}999}{2{\cdot}999}=3:1.$$

According to this law in aluminium carbide, aluminium and carbon must be in this ratio.

So, 4 parts by wt of aluminium carbide contain 3 parts by wt of aluminium.

∴ 100 parts by wt of aluminium carbide must contain $\frac{3\times100}{4}=75$ parts by wt of aluminium.

Percentage of aluminium in aluminium carbide is therefore 75.

(2) Ammonia contains 17·65% hydrogen, water contains 11·11% hydrogen and nitrogen trioxide 36·84% nitrogen. Show that these figures illustrate the law of equivalent weights. *I. I. T. 1964.*

In ammonia, 17·65 parts by wt of hydrogen combine with 82·35 parts by wt of nitrogen.

$\therefore$ in ammonia, 1 part by wt of hydrogen combines with

$\frac{82{\cdot}35}{17{\cdot}65} = 4{\cdot}665$ parts by wt of nitrogen.

In water, 11·11 parts by wt of hydrogen combine with 88·89 parts by wt of oxygen.

$\therefore$ in water, 1 part by wt of hydrogen combines with

$\frac{88{\cdot}89}{11{\cdot}11} = 8$ parts by wt of oxygen.

Ratio of different weights of nitogen and oxygen combined with equivalent weight of hydrogen $= 4{\cdot}665 : 8$

$$= \frac{4{\cdot}665}{4{\cdot}665} : \frac{8}{4{\cdot}665} = 1 : 1{\cdot}714 \approxeq 2 : 3.$$

Ratio of weights of nitrogen and oxygen in nitrogen trioxide according to the question $= 36{\cdot}84 : 63{\cdot}16$

$$= \frac{36{\cdot}84}{36{\cdot}84} : \frac{63{\cdot}16}{36{\cdot}84} = 1 : 1{\cdot}714 \approxeq 2 : 3.$$

Hence, the figures given in the question illustrate the law of equivalent weights.

[$\because$ equivalent wt of H = 1 ; equivalent wt of nitrogen = 5 ; equivalent wt of oxygen = 8.]

(3) Hydrogen sulphide contains 5·88% of hydrogen ; water contains 11·11% hydrogen ; sulphur dioxide contains 50% sulphur. Show that these figures illustrate the law of combining weights.

I. I. T. 1962.

In hydrogen sulphide, 5·88 gms of hydrogen combine with 94·12 gms of sulphur. $\therefore$ in hydrogen sulphide, 1 gm of hydrogen combines with $= \frac{94{\cdot}12}{5{\cdot}88} = 16{\cdot}061$ gms of sulphur.

In water, 11·11 gms of hydrogen combine with 88·89 gms of oxygen. $\therefore$ in water 1 gm of hydrogen combines with

$\frac{88{\cdot}89}{11{\cdot}11} = 8{\cdot}03$ gms of oxygen. $\because$ eq. wt of hydrogen = 1.

Ratio of different weights of sulphur and oxygen combined with equivalent weight of hydrogen $= 16{\cdot}061 : 8{\cdot}03$

$$= \frac{16{\cdot}061}{8{\cdot}03} : \frac{8{\cdot}03}{8{\cdot}03} \approx 2 : 1.$$

Ratio of weights of sulphur and oxygen in sulphur dioxide according to the question = 50 : 50 = 1 : 1.

Hence, these results show that the figures are in accordance with the law of reciprocal proportions.

(5) **The law of gaseous volume or Gay-Lussac's law** states that: when gases combine together they do so (i) in simple ratio by volume and (ii) the volume of the product if gaseous, also bears a simple relation to the volume of the reacting gases measured under the **same conditions of temperature and pressure.**

Illustrations :—(a) Hydrogen gas can combine with oxygen gas to form steam under the same conditions of temperature and pressure.

2 volumes of hydrogen combine with 1 volume of oxygen to produce 2 volumes of steam under the same conditions of temperature and pressure. The relation by volume amongst reactants and product is 2 : 1 : 2.

(b) 2 volumes of carbon dioxide combine with 1 volume of oxygen to form 2 volumes of carbondioxide under the same conditions of pressure and temperature. The relation by volume is 2 : 1 : 2.

(c) 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia under the same conditions of temperature and pressure. The relation by volume is 1 : 3 : 2.

(d) 1 volume of oxygen combines with 2 volumes of sulphur dioxide to form 2 volumes of sulphur trioxide under the same conditions of temperature and pressure. The relation by volume is 1 : 2 : 2.

(e) 1 volume of oxygen combines with 1 volume of nitrogen to form 2 volumes of nitric oxide under the same conditions of temperature and pressure. The relation by volume is 1 : 1 : 2.

(f) 1 volume of carbonmonoxide combines with 1 volume of steam to form 1 volume of carbondioxide and 1 volume of hydrogen under the same conditions of temperature and pressure. The relation by volume is 1 : 1 : 1 : 1.

Numerical example : All the problems are solved in Eudiometry (volume – volume calculation) chapter on the basis of the law of gaseous volume or Gay—Lussac's law.

Miscellaneous :

(1) Metal M and chlorine combine in different proportions to form two compounds A and B. The mass ratio M : Cl is 0·895 : 1 in A, and 1·791 : 1 in B. Which law of chemical combination does this example illustrate ? How ? *I. I. T. (Gp. B) 1969.*

This numerical example illustrates the law of multiple proportions. The reason is that the weights of metal (M) combining with the same weight of chlorine (Cl) in A and B are in the ratio $0{\cdot}895 : 1{\cdot}791 = \frac{0{\cdot}895}{0{\cdot}895} : \frac{1{\cdot}791}{0{\cdot}895} = 1 : 2$, which is a simple ratio.

(2) Two oxides of a metal (M), when heated to a constant weight in a current of hydrogen, gave 0·12585 gm and 0·2264 gm of water respectively per gm of the oxide used. If the formula for the latter oxide be given by *MO*, find that for the other.

West. Bengal. H. S. 1973.

18 gm water contain 16 gms of oxygen.

∴ 0·12585 gm of water contains $\frac{16 \times 0{\cdot}12585}{18}$

$= 0{\cdot}1118$ gms of oxygen.

So, in the first metal oxide, amount of oxygen $= 0{\cdot}1118$ gm ;

amount of metal $= 1 - 0{\cdot}1118 = 0{\cdot}8882$ gm.

In the first metal oxide, 0·1118 gm of oxygen combines with 0·8882 gm of metal.

∴ in the first metal oxide, 8 gms of oxygen combine with

$\frac{0{\cdot}8882 \times 8}{0{\cdot}1118} = 7{\cdot}944 \times 8$ gms of metal (*M*).

Again, 18 gms of water contain 16 gms of oxygen.

∴ 0·2264 gm of water contains $\frac{16 \times 0{\cdot}2264}{18} = 0{\cdot}2012$ gms.

of oxygen. So, in the 2nd metal oxide amount of oxygen = 0·2012 gm ; amount of metal = 1 − 0·2012 = 0·7988 gm. In the 2nd metal oxide, 0·2012 gm of oxygen combines with 0·7988 gm of metal.

∴ in the 2nd metal oxide, 8 gms of oxygen combine with $\frac{0{\cdot}7988 \times 8}{0{\cdot}2012} = 3{\cdot}970 \times 8$ gms of metal (M).

Ratio of different weights of metal (M) combined with equivalent weight of oxygen $= \frac{7{\cdot}944 \times 8}{3{\cdot}970 \times 8} = 7{\cdot}944 : 3{\cdot}970$

$$= \frac{7{\cdot}944}{3{\cdot}970} : \frac{3{\cdot}970}{3{\cdot}970} = 2 : 1.$$

Formulae of the two metal oxides are therefore M_2O, MO respectively. Formula of other is M_2O.

Problems for practice

1. How much silver nitrate should be allowed to react with 1·16 gms of sodium chloride so as to yield 1·70 gms of sodium nitrate and 2·87 gms of silver chloride ? It is supposed that the law of conservation of mass fully holds good. Ans. 3·41 gms.

2. 1·2375 gms of cupric oxide on being heated in a current of hydrogen gave 0·9882 gm of the metal. In a second experiment, 1·2969 gms of pure copper were dissolved in nitric acid, excess of the acid evapoated off and the residue ignited to constant weight. The residue (copper oxide) was 1·6828 gms. Show that these results illustrate the law of constant composition. *Punjab. U. I. Sc. 1963.*

3. Weight of copper oxide obtained by heating 2·16 gms of metallic copper with nitric acid and subsequent ignition was 2·70 gms. In another experiment, 1·15 gms of copper oxide on reduction yielded 0·92 gm of copper. Show that the results illustrate the law of definite proportions. *Punjab. H. S. 1965.*

4. Two elements (X) and (Y) combine with each other to form three compounds having 75·0%, 85·8% and 92·31% of (X).

Show that these results are in accordance with the law of multiple proportions. *Bombay.* U. *1962.*

5. A metal forms two oxides. One contains 63·64 percent of the metal and the other 46·67 percent of the metal. Show that these results are in accordance with the law of multiple proportions. *Bombay.* U. *1963.*

6. A metal is found to give two oxides ; on heating 1 gm of each in a current of hydrogen, 0·798 and 0·888 gm of the metal were obtained. Show that these results are in agreement with the law of multiple proportions. *Ranchi.* U. *Pre.* U. *1964.*

7. Two chlorides of a metal contain 35·9% and 52·8% of chlorine respectively. Show that the results are in accordance with the law of multiple proportions.

West Bengal H. S. 1963 (Comp.) ; 1966 **(*Comp*).**

8. Carbon forms two gaseous hydrides containing 75% and 80% of carbon respectively. Show that these compositions accord with the law of multiple proportions.

West Bengel H. S. 1964 (Comp'.

9. A metal forms two oxides. When 1 gm of each of the oxides is reduced, the weights of the metal produced are found to be 0·798 and 0·888 gm respectively. Show that the experimental results support the law of multiple proportions.

West Bengal H. S. 1968.

10. A certain metal forms two oxides, when 2 gms of the first oxide was heated in a stream of hydrogen 0 2517 gm of water was obtained while 1gm of the second oxide under similar condition gave 0·2264 gm of water. Show that the results illustrate the law of multiple proportion.

West Bengal E. Adn. T. E. 1969.

11. Two oxides of a metal, on analysis are found to contain 77·78% and 70·0% the metal. Show that these results support the law af multiple proportions. *West Bengal H. S. 1971.*

12. An element forms two oxides containing respectively

53·33 and 36·36 per cent of oxygen. Show that these figures illustrate the law of multiple proportions. *All India H. S. 1971.*

13. A metal is found to give two oxides ; on heating one gm of each in a current of hydrogen 0·798 ; 0·889 gms of metal were obtained. Show that the results are in agreement with the law of multiple proportions. *West Bengal Adn. T. E. E. 1974.*

14. Heating different oxides of lead in a current of hydrogen, following results were obtained : (i) 1·393 gms of litharge gave 1·293 gms of lead (ii) 2·173 gms of lead peroxide gave 1·882 gms of lead. (iii) 1·712 gms of red lead gave 1·552 gms of lead. Show that the results are in agreement with the law of multiple proportions. *West Bengal H. S. 1974* (Comp).

15. A metal has three oxides. One gm of each of them on reduction gave 0·928, 0·906 and 0·866 gm of metal respectively. Show that the results are in agreement with the law of multiple proportions. *W. B. H. S.* (Comp.) *1975.*

16. Three oxides of lead contained 92·85%, 90·63% and 86·51% of lead respectively. Shaw that these percentages are in accordance with the law of multiple proportions.

West Bengal H. S. Tech. 1974. W. B. H. S. 1977.

17. A metal is found to give two oxides, on heating one gramme of each in a current of hydrogen, 0·798 and 0·888 grammes of the metal were obtained. Show that the results are in agreement with the law of multiple proportions.

West Bengal Adn. T. E. (Medical) *1978.*

18. 1 gm hydrogen combines with 8 gms of oxygen to form water ; 2 gm hydrogen combine with 32 gms of sulphur to form sulphuretted hydrogen, and sulphur and oxygen combine in the ratio of 1 : 1 or 2 : 3. Show that these results are in agreement with the law of reciprocal proportions. *Punjab.* U. *I. Sc. 1961.*

19. 0·14 gm of an element *A* combines with 0·16 gm of an element B ; also 0·05 gm of another element C combines with 0·35 gm of A. Again, it is found that 0·2857 gm of C combines

with 2·2857 gms of B. Show that these figures illustrate the law of equivalent proportions. *Delhi. H. S. 1967.*

20. A metal (×) has two chlorides containing respectively 44·1% and 34·5% of ×. Calculate the weight of (×) which combines with 35·5 gms of chlorine in each compound. *Bombay.* U. *1965.* Ans. 28 ; 18·698.

21. 2·45 gms of $KClO_3$ yielded 1·49 gm of KCl and 672 ml of oxygen at N.T.P. These data are in accordance with which law ?

22. Water is 11·2% hydrogen and 88·8% oxygen ; hydrogen peroxide is 5·93% hydrogen and 94·07% oxygen. Show how these data illustrate the law of multiple proportions.

Hyderabad I. Sc. 1974.

23. On passing a stream of hydrogen gas over 2·173 gms of Litharge, 1·949 gms of lead peroxide and 2·315 gms of Red lead, 2·017 gms, 1·688 gms and 2·100 gms of Lead were left respectively. Show which law of chemical combination by weight do these data satisfy. *W. B. J. E. E.* 1977. Ans. Multiple proportion.

24. Chlorine and oxygen form two different compounds. One of them contains 81·6% and the other contains 59·7% of chlorine by weight. State the law of chemical combination which is in agreement with this experiment. *W.B.H.S.C. 1979* Ans. Law of multiple proportion.

25. The percentage compositions by weight of four compounds are nitrogen 11.6, chlorine 88·4 (b) nitrogen 46·7, oxygen 53·3 (c) Oxygen 22·2, iron 77·8 (d) iron 44·1, chlorine 55·9. Show that these compositions are in accordance with the law of reciprocal proportions.

26. A certain metal forms two chlorides which contain 85·2% and 65·8% of the metal. State the law with which the above data are consistent. *Roorkee Adn. Test E. 1974.*

Ans. Law of multiple proportion.

CHAPTER 7

Problems on Chemical equation (weight to weight and weight to volume calculations).

A chemical equation represents the relative weights of the reactants and the products involving in the chemical reaction. Since 1 gm molecular weight of a gas occupies a volume of 22·4 litres at S. T. P., the molecular formula of a gaseous substance also indicates 22·4 litres of it at S. T. P. as well as one gm molecular weight of it. For example, the molecular formula CO_2 indicates 44 gms of carbon dioxide according to weight in gms and 22·4 litres of carbon dioxide at S. T. P by volume.

Some important points on the procedure of calculation.

(i) Write first a balanced equation for the relevant chemical reaction ; (ii) Write down the product of the molecular weight and the number of moles of each relevant substance below its formula. These numbers written below the chemical formulae of various substances will indicate their relative weights ; (iii) If the calculation involves volume, write down the product of 22·4 and the number of its moles below the molecular formula of the gaseous substance. The number will indicate the volume in litres of the substance at S. T. P.

Solved problems on chemical equation based on weight to weight calculation.

1. When a mixture of NaBr and NaCl is repeatedly digested with sulphuric acid, all the halogens are expelled and Na_2SO_4 is formed quantitatively. With a particular mixture it was found that the weight of Na_2SO_4 obtained was precisely the same as the weight of NaBr—NaCl mixture taken. Calculate the ratio of the weights of NaCl and NaBr in the mixture. *I.I.T.* (*Group A*) *1970*

Equations for the relevant chemical reactions are given below.

$2NaBr + H_2SO_4 \rightarrow Na_2SO_4 + 2HBr$ ... (i)

$2(23+80) = 206$ gms 142 gms

$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$ ... (ii)

117 gms 142 gms

Let the amount of the mixture of NaBr and NaCl = 1 gm.

a gm is supposed to be the amount of NaBr in the mixture.

$\therefore$ amount of NaCl in the mixture $= (1-a)$ gm and the total amount of Na_2SO_4 obtained in the above chemical reactions = 1 gm by the question. From quation (i) ; 206 gm NaBr yield 142 gm Na_2SO_4.

$\therefore$ a gm NaBr yields $\frac{142a}{206}$ gm Na_2SO_4.

From equation (ii), 117 gm NaCl yield 142 gm Na_2SO_4.

$\therefore$ $(1-a)$ gm NaCl yields $\frac{142(1-a)}{117}$ gm Na_2SO_4.

Total amount of Na_2SO_4 obtained $= \frac{142a}{206} + \frac{142(1-a)}{117}$.

According to the question, $\frac{142a}{206} + \frac{142(1-a)}{117} = 1$.

$\therefore$ $a = 0{\cdot}4$ gm. Amount of NaBr = 0·4 gm ; amount of NaCl $= (1-a)$ gm $= (1-0{\cdot}4)$ gm = 0·6 gm. Ratio of the amounts of NaCl and NaBr in the mixture = 0·6 : 0·4

$$= \frac{0{\cdot}6}{0{\cdot}4} : \frac{0{\cdot}4}{0{\cdot}4} = 1{\cdot}5 \times 2 : 1 \times 2 = 3 : 2.$$

2. How much potassium permanganate and potassium dichromate would be needed to oxidise 1 gm mole of ferrous sulphate to ferric state in presence of acid ? (K = 39, Mn = 55, Cr = 52, Fe = 56, O = 16) *Ranchi. University, 1970.*

One mole of ferrous sulphate transfers only one electron in the reaction ; hence its equivalent weight is equal to its molecular weight i.e., 1 gm mole of ferrous sulphate = 1 gm equivalent of ferrous sulphate because

$$\text{equivalent weight} = \frac{\text{molecular weight}}{\text{number of electron transferred}}.$$

Here, equivalent weight of ferrous sulphate $= \frac{\text{mol. wt}}{1}$ as

$Fe^{2+} - e \rightarrow Fe^{3+}$ (one electron transferred).
(ferrous) (ferric)

Again, 1 gm equivalent of ferrous sulphate is oxidised to ferric state in presence of acid by 1 gm equivalent of potassium permanganate (an oxidising agent) and by 1 gm equivalent of potassium dichromate (an oxidising agent) by the law of equivalent proportions. Hence, amount of potassium permanganate as well as dichromate needed = 1 gm eq wt.

Equivalent wt of $K_2Cr_2O_7 = \frac{\text{mol. wt of } K_2Cr_2O_7}{6}$ as

$K_2Cr_2O_7 \rightleftharpoons 2K^{1+} + Cr_2O_7^{2-}$;

$Cr_2O_7^{2-} + 14H^{1+} + 6e \rightarrow 2Cr^{3+} + 7H_2O$ (Sixelectron transferred)

$\therefore$ 1 gm equivalent of $K_2Cr_2O_7 = \frac{294}{6} = 49$ gms.

Equivalent weight of $KMnO_4$

$= \frac{\text{molecular weight of } KMnO_4}{5}$ as

$KMnO_4 \rightleftharpoons K^{1+} + MnO_4^{1-}$; $MnO_4^{1-} + 8H^{1+} + 5e \rightarrow Mn^{2+} + 4H_2O$ (five electron transferred)

$\therefore$ 1 gm equivalent of $KMnO_4 = \frac{158}{5} = 31{\cdot}6$ gms.

Here, ferrous sulphate is oxidised and at the same time potassium dichromate and potassium permanganate are reduced.

3. 25·4 gms of iodine and 14·2 gms of chlorine are made to react completely to yield a mixture of ICl and ICl_3. Calculate the ratio of the moles of ICl and ICl_3 formed.

I. I. T (Group B) 1970.

$I_2 + 2Cl_2 \longrightarrow ICl + ICl_3$
1 mole 2 moles 1 mole 1 mole

[At wt of iodine = 127 ; at wt of chlorine = 35·5]

$\frac{25{\cdot}4}{2 \times 127}$ mole $\frac{14{\cdot}2}{3{\cdot}55 \times 2}$ mole

$\because$ 1 mole of iodine = 2 atoms of iodine ; 1 mole of chlorine = 2 atoms of chlorine and number of moles $= \frac{\text{wt}}{\text{mol. wt.}}$

Number of moles of ICl formed due to $\frac{25.4}{2\times127}$ mole of iodine $=\frac{25.4}{2\times127}$, according to above equation.

$\because$ 1 mole iodine $\equiv$ 1 mole ICl.

Number of moles of ICl_3 formed due to $\frac{25.4}{2\times127}$ mole of iodine $=\frac{25.4}{2\times127}$, according to the equation mentioned above.

$\because$ 1 mole iodine $\equiv$ 1 mole ICl_3.

Number of moles of ICl formed due to $\frac{14.2}{35.5\times2}$ mole of chlorine $=\frac{14.2}{35.5\times2\times2}$ $\quad\because$ 1 mole chlorine $\equiv\frac{1}{2}$ mole ICl.

Number of moles of ICl_3 formed due to $\frac{14.2}{35.5\times2}$ mole of chlorine $=\frac{14.2}{35.5\times2\times2}$ $\quad\because$ 1 mole chlorine $\equiv\frac{1}{2}$ mole ICl_3.

$\therefore$ total number of moles of ICl formed due to iodine as well as chlorine $=\frac{25.4}{2\times127}+\frac{14.2}{35.5\times2\times2}$ and total number of moles of ICl_3 formed due to iodine as well as chlorine

$$=\frac{25.4}{2\times127}+\frac{14.2}{35.5\times2\times2}.$$

Ratio of number of moles of ICl and ICl_3 formed

$$=\frac{\frac{25.4}{2\times127}+\frac{14.2}{35.5\times2\times2}}{\frac{25.4}{2\times127}+\frac{14.2}{35.5\times2\times2}}=1:1.$$

4. 1·84 gms of a mixture of $CaCO_3$ and $MgCO_3$ are strongly heated till no further loss of weight takes place. The residue weighs 0·96 gm. Calculate the percentage composition of mixture. [Mg—24 ; Ca—40 ; C—12 ; O—16]

Calcutta University B. Sc. 1971, 1976 ; Ranchi University (Bihar) 1979.

$$\begin{array}{lll} CaCO_3 & \rightarrow & \downarrow CaO + \uparrow CO_2 \\ 40+12+48 & & 40+16 \\ =100\text{ gms} & & =56\text{ gms (residue)} \end{array}$$

Let the amount of $CaCO_3$ in the mixture $= a$ gm.

$\therefore$ the amount of $MgCO_3$ in the mixture $= (1{\cdot}84 - a)$ gm.

100 gm $CaCO_3$ on heating give off 56 gms of CaO as residue.

$\therefore$ a „ „ „ „ „ „ $\dfrac{56a}{100}$ „ „ „ „ „.

$$\begin{array}{llll} MgCO_3 & \rightarrow & \downarrow MgO & + \uparrow CO_2 \\ 24+12+48 & & 24+16 & \\ =84 \text{ gms} & & =40 \text{ gms (residue)} & \end{array}$$

84 gm $MgCO_3$ on heating give off 40 gms of MgO as residue.

$\therefore$ $(1{\cdot}84 - a)$ „ „ „ „ $\dfrac{40(1{\cdot}84-a)}{84}$ „ „ „.

$$\frac{56a}{100}\text{ gm} + \frac{40(1{\cdot}84-a)}{84}\text{ gm} = 0{\cdot}96 \text{ gm by the question.}$$

$\therefore$ $a = 1$ gm. Amt. of $CaCO_3 = 1$ gm ; amt. of $MgCO_3$ $= (1{\cdot}84 - 1)$ gm $= 0{\cdot}84$ gm.

$$\% \text{ of } CaCO_3 = \frac{100 \times 1}{1{\cdot}84} = 54{\cdot}347 ;$$

% of $MgCO_3 = 100 - 54{\cdot}347 = 45{\cdot}653$.

N. B. Dolomite mainly contains $CaCO_3$ and $MgCO_3$.

5. How much MnO_2 and how much hydrochloric acid containing 33%HCl, would be required to furnish chlorine necessary to convert 40 gms of KOH into chlorate and chloride ?

Ranchi University, 1971 ; *Patna*. U. 1976.

$$\begin{array}{lllll} 6KOH & + \; 3Cl_2 & \rightarrow KClO_3 & + \; 5KCl & + \; 3H_2O \\ 6(39+16+1) & 3(35{\cdot}5+35{\cdot}5) & \text{Potassium} & \text{Potassium} & \\ =6\times 56 \text{ gms} & =3\times 71 \text{ gms} & \text{chlorate} & \text{chloride} & \end{array}$$

6 × 56 gms of KOH are converted into chlorate and chloride by combining with 3 × 71 gms of chlorine.

$\therefore$ 40 gms of KOH are converted into chlorate and chloride by combining with $\dfrac{3\times 71\times 40}{6\times 56} = 25{\cdot}357$ gms of chlorine.

$$\begin{array}{llll} MnO_2 + & 4HCl \rightarrow & MnCl_2 + \uparrow & Cl_2 + 2H_2O \\ 87 \text{ gms} & 146 \text{ gms} & & 71 \text{ gms} \end{array}$$

71 gm chlorine, obtained from 87 gm MnO_2 on reacting with HCl.

25·357 „ „ „ $\frac{87\times 25\cdot357}{71}=31.071$ „ „ .

$\therefore$ amount of MnO_2 required $=31\cdot071$.

Again, 71gm chlorine, obtained from 146 gm pure HCl on reacting with MnO_2.

25·357 „ „ „ $\frac{146\times 25\cdot357}{71}=52\cdot142$ „ „

According to the question, 33 gm pure HCl come from 100 gm impure hydrochloric acid.

$\therefore$ 52·142 gm pure HCl come from $\frac{100\times 52\cdot142}{33}=158$ gm.

impure hydrochloric acid. Amount of 33% hydrochloric acid $=158$ gms.

6. 5 gms of a mixture of potassium chloride and potassium chlorate on ignition left 4 gms of the chloride as residue. Find the percentage of potassium chlorate in the mixture.

Ranchi University, 1974.

Let the amount of potassium chlorate in the mixture be *a* gms. $2KClO_3 \rightarrow \downarrow 2KCl + \uparrow 3O_2$

$2\times 122\cdot5$gms $2\times 74\cdot5$ gms

$2\times 122\cdot5$ gm $KClO_3$ on ignition left $2\times 74\cdot5$ gm KCl.

$\therefore$ a „ „ „ „ „ $\frac{2\times 74\cdot5a}{2\times 122\cdot5}$ „ „ .

$\left(\frac{74\cdot5a}{122\cdot5}\right)$ gm $+(5-a)$gm $=4$ gm by the question.

$\therefore$ $a=2\cdot551$ gms ; % of $KClO_3=\frac{2\cdot551\times 100}{5}=51\cdot02$.

7. A mixture of FeO and Fe_3O_4 when heated in air to a constant weight, gains 5% in its weight. Find the composition of the initial mixture. *I.I.T.* (*Group A*) 1978.

Amount of initial mixture (say) $=100$ gms. Let the amount of FeO in the mixture $=X$ gms. $6FeO+O_2=2Fe_3O_4$

$6(56+16)=432 \quad 2(56\times3+16\times4)=464$

$\therefore$ X gm FeO yield $\frac{464X}{432}=1{\cdot}074X$ gm Fe_3O_4.

Hence, $1{\cdot}074X+100-X=105$. $X=67{\cdot}56$ gms.

$\therefore$ percentage of FeO in the initial mixture$=67{\cdot}56$ and percentage of Fe_3O_4 in the initial mixture$=100-67{\cdot}56=32{\cdot}44$.

Solved problems on chemical equation based on weight to volume calculation.

8. How much ammonia by weight and volume at 20°C and 750 mm will be obtained from 8·5 gms of sodium nitrate when the latter is heated with zinc and sodium hydroxide solution ?

Ranchi University Pre. U. *1965 ; 1969.*

$NaNO_3+4Zn+7NaOH\rightarrow\uparrow NH_3+4Na_2[ZnO_2]+2H_2O$

$23+14+16\times3=85$ gms 17 gms (22·4 litres at N.T.P)

85 gms of $NaNO_3$ on heating with Zn and NaOH yield 17 gm NH_3.

$\therefore$ 8·5 " " " " " " " $\frac{17\times8.5}{85}=1{\cdot}7$ " "

Again, 85 gm $NaNO_3$ on heating with Zn and NaOH yield 22·4 lit NH_3 at N.T.P.

$\therefore$ 8·5 gm " " " " " $\frac{22{\cdot}4\times8{\cdot}5}{85}=224$ " "

We have, $\frac{P_0V_0}{T_0}=\frac{P_1V_1}{T_1}$;

$$\frac{1\times224}{273}=\frac{\frac{750}{760}V_1}{273+20} \quad \therefore \quad V_1=243{\cdot}615 \text{ lit.}$$

9. What will be the proportion of SO_2 at N.T.P. when 10 gms of Cu and 10 gms of S are separately treated with conc. H_2SO_4 (Cu=63 ; S=32) ? *West Bengal Engineering Admission test.* E. 1969.

$Cu+2H_2SO_4\rightarrow CuSO_4+2H_2O+SO_2$

63 gms 22·4 litre at N.T.P.

63 gm Cu on treatment with conc. H_2SO_4 produce
22·4 lit. SO_2 at N.T.P.

∴ 10 gm ,, ,, ,, ,, ,, $\frac{22\cdot4\times10}{63}$,, ,,

$S+2H_2SO_4\rightarrow3SO_2+2H_2O$

32 gms (3×22·4) litres at N.T.P.

∵ 32 gm S on treatment with conc. H_2SO_4 yield
(3×22·4) lit. SO_2 at N.T.P.

∴ 10 ,, ,, ,, ,, ,, $\frac{3\times22\cdot4\times10}{32}$,, ,,

Proportion of SO_2 evolved at N.T.P. in two different reactions

$$=\frac{\frac{22\cdot4\times10}{63}}{\frac{3\times22\cdot4\times10}{32}}=\frac{32}{189}=32:189=\frac{32}{32}:\frac{189}{32}=1:5\cdot906.$$

10. What volume of air containing 21% oxygen by volume is required to burn 1000 gms of sulphur containing 4% non-combustible matter. *West Bengal E. Adn. T. E. 1971.*

According to the question, 100 gm *S* contain 4 gm non
combustible matter.

∴ 1000 ,, ,, $\frac{4\times1000}{100}=40$ gm,, ,,

∴ amount of combustible sulphur = 960 gm.
[∵ 1000 − 40 = 960]

$S+O_2\rightarrow SO_2$

32 gms 22·4 litres at N. T. P.

32 gm S combine with 22·4 lit. Oxygen at N. T. P.

960 ,, ,, ,, $\frac{22\cdot4\times960}{32}=672$,, ,,

Now, 21 cc oxygen remain in 100 cc air at N. T. P.

∴ 672×1000 cc ,, ,, $\frac{100\times672000}{21}$
= 3200 litres of air at N. T. P.

11. Oxygen obtained by heating 12·25 gms of potassium chlorate is passed over 5 gm pure, dry and heated carbon. A part

of carbon burns to carbon dioxide. What is the volume of this CO_2 formed at 27°C and 750 mm pressure and what is the weight of residual carbon ? Assume that no carbon monoxide is formed. (K—39, Cl—35·5, O—16) *Calcutta University B.Sc., 1972.*

$$2KClO_3 \rightarrow \downarrow 2KCl + \uparrow 3O_2$$

145 gms 96 gms

∴ 12·25 gm $KClO_3$ on decomposition give off $\frac{96 \times 12{\cdot}25}{145}$

$= 8{\cdot}11$ gms of oxygen.

$$C + O_2 \rightarrow CO_2$$

12 gms 32 gms 22·4 litres at N. T. P.

32 gm oxygen combine with 12 gm carbon

∴ 8·11 " " $\frac{12 \times 8{\cdot}11}{32} = 3{\cdot}041$ gm carbon.

Residual amount of carbon $= 5 - 3{\cdot}041 = 1{\cdot}959$ gms.

32 gm oxygen produce 22·4 litre carbon dioxide at N.T.P.

∴ 8·11 " " $\frac{22{\cdot}4 \times 8{\cdot}11}{32} = 5{\cdot}677$ " " .

We have, $\frac{P_0V_0}{T_0} = \frac{P_1V_1}{T_1}$; $\frac{1 \times 5{\cdot}677}{273} = \frac{\frac{750}{760} \times V_1}{273+27}$

∴ $V_1 = 6{\cdot}321$ lits.

∴ V_1 = Volume of carbondioxide at 750 mm pressure at 27°C = 6·321 litres.

12. 5·08 gms of iodine held in suspension in water are slowly acted upon by 460 cc of sulphuretted hydrogen measured at N. T. P. What weight of sulphur will be liberated ? (I=127, S=32) *Ranchi University, 1973A.*

$$I_2 + H_2S \rightarrow 2HI + S$$

254 gms 22·4 lits at N. T. P. 32 gms

∴ 5·08 gm iodine combine with $\frac{22{\cdot}4 \times 5{\cdot}08 \times 1000}{254}$

$= 448$ cc H_2S at N. T. P.

Excess of $H_2S = 460$ cc $- 448$ cc $= 12$ cc.

254 gm iodine displace 32 gm S from H_2S.

$\therefore$ 5·08 " " $\frac{32\times5\cdot08}{254}=0\cdot64$ gm " "

Amount of S, liberated = 0·64 gm.

13. One gm of a mixture of $CaCO_3$ and $MgCO_3$ gives 240 cc of CO_2 at N. T. P. Calculate the percentage composition of the mixture. *Kurukshetra.* U. *1967* ; *Ranchi.* U. *1975A* ; *W. Bengal Adn. T. E. (Medical) 1978.*

$$CaCO_3 \rightarrow \downarrow CaO + \uparrow CO_2$$

100 gms 22400 cc at N. T. P.

Let the amount of $CaCO_3$ in the mixture = a gm.

$\therefore$ the amount of $MgCO_3$ in the mixture = $(1-a)$ gm.

100gm $CaCO_3$ on heating give off 22400cc CO_2 at N.T.P.

$\therefore$ a " " " gives off $\frac{22400a}{100}$ " ".

$$MgCO_3 \rightarrow \downarrow MgO + \uparrow CO_2$$

84 gms 22400 cc at N. T. P.

84 gm $MgCO_3$ on heating give off 22400 cc CO_2 at N.T.P.

$\therefore$ $(1-a)$ gm " " gives off $\frac{22400(1-a)}{84}$ " ".

$\frac{22400a}{100}$ cc $+\frac{22400(1-a)}{84}$ cc = 240 cc at N.T.P. by the question.

$\therefore$ $a=0\cdot6249$ gm. Amount of $CaCO_3=0\cdot6249$ gm ; amount of $MgCO_3=(1-0\cdot6249)$ gm $=0\cdot3751$ gm.

% of $CaCO_3=\frac{100\times0\cdot6249}{1}=62\cdot49$;

% of $MgCO_3=100-62\cdot49=37\cdot51$.

14. A dilute solution of sulphuric acid contains 65% of the acid by weight and its density is 1·55. Calculate the volume of hydrogen liberated at 27°C and 750 mm pressure when 750 gms of zinc mixed with one litre of this solution. (Zn = 65)

W. Bengal H. S. 1975.

100 gm dilute sulphuric acid contain 65 gm H_2SO_4
by the question.

∴ $1000 \times 1·55$,, ,, ,, $\frac{65 \times 1000 \times 1·55}{100}$
$= 1007·5$,, ,, .

∵ $\text{density} = \frac{\text{amount}}{\text{volume}}$; $15·5 = \frac{\text{amount}}{1000}$

∴ amount of dilute sulphuric acid $= 1000 \times 1·55$ gms.

We have, $Zn + H_2SO_4 \rightarrow ZnSO_4 + \uparrow H_2$
65 gms 98 gms 22·4 litres at N. T. P.

65 gm Zn react with 98 gm H_2SO_4

∴ 750 ,, ,, ,, ,, $\frac{98 \times 750}{65} = 1130·769$,, ,, .

This amount of H_2SO_4 is greater than that of the given amount (1007·5).

Again, 98 gm H_2SO_4 react with 65 gm Zn.

∴ 1007·5 ,, ,, ,, $\frac{65 \times 1007·5}{98} = 668·239$ gm Zn.

This amount (668·239) has been completely reacted with 1007·5 gms of H_2SO_4.

∴ amount of Zn remains unreacted = 750 gms − 668·239 gms 81·761 gms.

Now, 98 gm H_2SO_4 yield 22·4 litre hydrogen at N.T.P.

∴ 1007·5 ,, ,, $\frac{22·4 \times 1007·5}{98} = 230·285$,, ,, ,,

We have, $\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$;

$$\frac{1 \times 230·285}{273} = \frac{\frac{750}{760} V_1}{273+27} \quad \therefore \quad V_1 = 256·434 \text{ lits.}$$

15. A sample of gaseous hydrocarbon occupying 1·12 litres at N.T.P, when completely burnt in air produced 2·2 gms of CO_2 and 1·8 gms of H_2O. Calculate the weight of the compound

taken and the volume of O_2 at N.T.P required for its burning. Find the molecular formula of the hydrocarbon.

I. I. T. (group A) 1978.

44 gm CO_2 contain 12 gm carbon.

$\therefore$ 2·2 gm " " $\frac{12 \times 2{\cdot}2}{44} = 0{\cdot}6$ gm carbon.

18 gm H_2O contain 2 gm hydrogen.

$\therefore$ 1·8 " " " $\frac{2 \times 1{\cdot}8}{18} = 0{\cdot}2$ gm hydrogen.

We have, $PV = nRT$; $1 \times 1{\cdot}12 = n \times 0{\cdot}0821 \times 273$.

$\therefore$ $n = 0{\cdot}0499$ mole.

So, 0·0499 mole hydrocarbon contains $\frac{0{\cdot}6}{12}$ atom of carbon and $\frac{0{\cdot}2}{1}$ atom of hydrogen. $\because$ at. wt of $C = 12$; at. wt of $H = 1$.

$\therefore$ 1 mole hydrocarbon contains $\frac{0{\cdot}6}{12 \times 0{\cdot}0499} = 1$ atom of carbon and $\frac{0{\cdot}2}{0{\cdot}0499} = 4$ atoms of hydrogen.

Molecular formula of hydrocarbon is therefore CH_4.

22·4 litre CH_4 (methane) at N.T.P weigh 16 gms.

$\therefore$ 1·12 " " " " " $\frac{16 \times 1{\cdot}12}{22{\cdot}4} = 0{\cdot}8$ gm

$\because$ 1 gm mole $CH_4 = 16$ gms ; molecular weight of $CH_4 = 16$.

We know, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

16 gms 2 × 22·4 lits at N.T.P.

16 gm CH_4 combine with 44·8 litre oxygen at N.T.P.

$\therefore$ 0·8 " " combines " $\frac{44{\cdot}8 \times 0{\cdot}8}{16}$

$= 2{\cdot}24$ litre oxygen at N.T.P.

Problems for practice

1. How much iron can be theoretically obtained by the reduction of 1 K gm of Fe_2O_3. *Delhi. U. Pre. Medical. 1961.*

Ans. 700 gms.

2. A mixture of sodium iodide and sodium chloride gave with sulphuric acid, sodium sulphate equal to the weight of the original mixture taken. Fied the percentage composition of the mixture. *Punjab. U. I. Sc. 1962.*

Ans. %NaI=28·85 ; %NaCl=71·15.

3. Hydrogen is generated by the action of steam on hot magnesium. Calculate the weight of magnesium that will be required to produce just sufficient hydrogen to combine with all the oxygen that can be obtained by the complete decomposition of 24·5 gms of $KClO_3$. *Delhi H. S. 1966.* Ans. 24·33 gms.

4. What minimum weight of water is needed to slake 1 kg of quicklime, assuming no loss of evaporation ? *Senior Cambridge. 1966.* Ans. 11·25 gms.

5. One gm of a miture of KCl and NaCl on treatment with excess of $AgNO_3$ gave 2 gms of AgCl. What was the percentage composition of the two salts in the original mixture ? *Punjab. U. Intermediate Science. 1969.* Ans. %NaCl=48·50 ; %KCl=51·50.

6. What weight of calcium oxide will be formed on heating 19·3 gms of calcium carbonate. *All India H. S. 1971.*

Ans. 10·80 gms.

7. One litre of an acidified solution of $KMnO_4^-$ containing 15·8 gms of $KMnO_4$ is decolourised by passing sufficient amount of SO_2. If the SO_2 is produced by roasting of iron pyrites (FeS_2), what will be the amount of pyrites required to produce the necessary amount of SO_2 ? *I. I. T. (group A). 1974.*

Ans. 15 gms.

8. Calculate the weight of lime (CaO) that can be prepared by heating 200 kg of lime stone ($CaCO_3$) which is 95% pure. (C=12, O=16, Ca=40) *I. I. T. (group B) 1975.* Ans. 106·4 kg.

9. How much of oxygen is there in 10 gms of potassium chlorate ? (K=39 ; Cl=35·5) *West Bengal H. S.C. (vocational). 1978.* Ans. 3·98 gms.

10. Calculate how much of acetic acid is obtained by oxidation of 8 gms of ethyl alcohol. *Hyderabad I. Sc. 1976.*

Ans. 10·4348 gms.

[Hint. $C_2H_5OH + O_2 = CH_3COOH + H_2O$.]

11. Igniting MnO_2 in air converts it quantitatively to Mn_3O_4. A sample of pyrolusite is of the following composition : MnO_2, 80% ; SiO_2 and other inert constituents, 15% ; rest being water. The sample is ignited in air to constant weight. What is the percentage of Mn in the ignited sample ? *I. I. T. (group A) 1978*

[$3MnO_2 \rightarrow Mn_3O_4 + O_2$] Ans. 59·3%.

12. What volume of the gaseous product measured at 750mm pressure and 17°C will be obtained by heating 0·8 gm of ammonium nitrate ? Ans. 241·1cc.

13. How much marble of 90% purity would be required to prepare 4·5 litres of CO_2 at N.T.P when the marble is acted upon by dilute hydrochloric acid ? *Agra.* U. *Pre. Medical.* 1967.

Ans. 22·32 gms.

14. What volume of oxygen measured at S. T. P will be obtained by heating 0·85 gm of sodium nitrate ? *Bombay.* U. *1967.*

Ans. 0·112 litre.

15. Brass is an alloy of copper and zinc. A sample of brass weighing 5·793 gm when, treated with an excess of dilute sulphuric acid gives 324 ml. of dry hydrogen at 20°C and 750 mm pressure. What is the percentage by weight of copper in the alloy ? *I. I. T. (GP. B) 1968.* %Zn = 14·975 ; %Cu = 85·025.

16. 10 gms of a mixture of ferrous sulphide and iron gave on treatment with dilute sulphuric acid 3·36 litres of mixed gases at N.T.P. Find the percentage composition of the mixture. (Fe = 56, S = 32) *Ranchi.* U. *1963, 1969A.*

Ans. %FeS = 43·8 ; %Fe = 56·2.

17. 20·95 litres of nitrous oxide at 17°C and 770 mm pressure weigh 3·93 gms. What is the weight of 500 cc of this gas at N.T.P. ? *West Bengal Joint Entrance. E. 1971.* Ans. 0·0983 gm.

18. One gm of an alloy of aluminium and magnesium reacts with excess hydrochloric acid to form aluminium chloride, magnesium chloride and hydrogen. The hydrogen, collected over mercury at 0°C, occupied 1200 ml at 699 mm Hg. What is the composition of the alloy ? *I. I. T.* (*Gp. B*). 1971.

Ans. %Al=54·77 ; %Mg=45·23.

19. How much sulphuric acid would be needed to neutralise ammonia produced from 107 gms of pure NH_4Cl ? What would be the volume of ammonia, if liberated and collected at 37°C and 760 mm and if the vapour tension of the liquid over which ammonia is collected be 2·3 mm ? *Ranchi.* U. *Pre.* U. *1971 Sup.*

Ans. 98 gms ; 51·02 litres.

20. What volume of carbon dioxide gas will be evolved at N.T.P by heating 7 3 gms of $Mg(HCO_3)_2$? *Punjab H. S. 1972.*

Ans. 2·24 litres.

21. What weight of pure MnO_2 will be required to produce 100 liters of Cl_2 at 37°C and 750 mm pressure by reaction with excess HCl ? (At. wt of Mn=55). *West Bengal Joint Entrance* E. *1974.*

Ans. 348·784 gms.

22. How many gms of calcium carbonate will be required for reacting with excess of dilute hydrochloric acid to liberate 560 cc carbon dioxide at N.T.P ? [Ca=40 ; C=12] *West Bengal H. S.* Tech. *1975.*

23. How many litres of oxygen at N.T.P are required to burn completely 2·2 gms of propane, C_3H_8 ? [At. wt : H=1, C=12] *I. I. T.* (*Gp. B*) 1976.

Ans. 5·6 litres.

24. How much of pure calcium carbonate and hydrochloric acid solution containing 22% of the acid by weight are required to give one litre of carbon dioxide gas at 27°C and 760 mm pressure ? How much of pure carbon will be needed to produce the same amount of carbon dioxide ? (Ca=40, Cl=35·5) *West Bengal H. S. 1976.* Ans. 4·0625 gm $CaCO_3$; 13·48 gm 22% HCl.

25. How much potassium chlorate will be required to yield

123 cc Oxygen at 27°C and 760 mm pressure. (K=39, Cl=35·5, O=16) *West Bengal H. S. 1977.* Ans. 0·2415 gm.

26. What will be the volume in cc of 8 gms of oxygen at N. T. P. ? *West Bengal H. S. C. (Vocational) 1978.* Ans. 5599 cc.

27. What weight of hydrogen peroxide labelled '12 volumes' will be necessary to have 4360 cc of dry oxygen at 10°C and 500 mm pressure ? Ans. 8·397 gms. Hints. '12 volumes' means 1 cc of H_2O_2 gives 12 cc Oxygen at S. T. P.

28. What volume of dry carbon dioxide measured at 27°C and 750 mm pressure is liberated, when 250 gms of pure calcium carbonate is treated with excess of hydrochloric acid. *Hyderabad. I. Sc. 1973.* Ans. 647·3 cc.

29. The hydrogen liberated by the reaction of 0·8 gm of Mg with dil H_2SO_4 was collected over water in the laboratory at 27°C and 756 mm pressure. Find its volume. *Hyderabad. I. Sc. 1975.* Ans. 854·5 cc.

30. Calcium carbonate decomposes according to the equation $CaCO_3 \rightarrow CaO + CO_2$. How much of $CaCO_3$ is required to be decomposed to give CO_2 which compressed in a cylinder at 5 atmosphere pressure at 18°C occupies. *Hyderabad. I. Sc. 1976.* Ans. 100 gms. Hints. Use $PV = RT$ for 1 mole CO_2. Find out 'V'.

31. On heating 4·90 gm $KClO_3$ shows a weight loss of 0·384 gm. What percentage of original $KClO_3$ has decomposed ? Calculate the volume of oxygen liberated at N. T. P. Ans. 92·44% ; 1·244 lit. *Hyderabad. 1974.*

32. Oxygen liberated by heating 0·02 mole of potassium chlorate is passed over 0·2 gm atom of pure, dry and heated carbon. A portion of carbon burns to carbon dioxide. What is the volume of this carbon dioxide formed at 27°C and 750 mm pressure, and what is the weight of residual carbon ? Assume that no carbon monoxide is produced during the reaction and the whole of the liberated oxygen took part in the reation. [K=39, Cl=35·5] *Calcutta U. B. Sc. 1977.*

Problem is solved on the basis of molar concept

$2KClO_3 \rightarrow 2KCl + \uparrow 3O_2$

2 mole $KClO_3$ produce 3 moles of oxygen

∴ 0·02 " produces $\frac{3}{2}\times 0{\cdot}02 = 0{\cdot}03$ mole of oxygen

$O_2 + C \rightarrow CO_2$

1 mole 1 gm atom 22·4 lit.

1 mole O_2 combines with 1 gm atom C

∴ 0·03 " " " 0·03 " "

Residual carbon in gm atom = 0·2 − 0·03 = 0·17.

" " in gms = 0·17 × 12 = 1·44 gms

∵ 1 gm atom C = 12 gms.

1 mole O_2 yields in combination with C, 22·4 litre CO_2 at N.T.P.

0·03 " " " " " " 22·4 × 0·03 = 0·672 " "

We have, $$\frac{P_0V_0}{T_0}=\frac{P_1V_1}{T_1} \quad \text{or} \quad \frac{1\times 0{\cdot}672}{273}=\frac{\frac{750}{760}V_1}{273+27}$$

∴ $V_1 = 0{\cdot}748$ lit at 27°C and 750 mm pressure.

Try to solve without molar corcept.

33. 3 gms of a mixture of anhydrous sodium carbonate and sodiumbicarbonate lost 0·348 gm on heating. Calculate the % of anhydrous carbonate in the mixture. [Na = 23 ; C = 12 ; O = 16].

Magadh U. 1973A ; *Ranchi U. 1963A, 1974A.* Ans. 68·56%.

34. For the preparation of FeS, 3 parts of iron filings are heated with 2 parts of S. The product from such a process is found to contain 60% of FeS. Calculate the compn. of the product. *Ranchi U. 1976A.* Ans. 60% FeS ; 18·2% S ; 21·8% Fe.

35. Calculate the wt of ammonium chloride required to give 10 litres of ammonia gas, measured at N. T. P. *Bhagalpur U. 1974A.* Ans. 23·88.

36. Calculate the wt of $KClO_3$ which when heated will liberate enough oxygen to react completely with hydrogen obtained by the action of dil H_2SO_4 on 6·5 gms of zinc. [K = 39 ; Cl = 35·5 ; O = 16 ; Zn = 65·5] *Ranchi.* U. *1974S.* Ans. 4·052.

37. What weight of $KClO_3$ will be required to get 5 gms of oxygen ? *R.* U. *1975S.* Ans. 12·76.

38. Calculate the amount of Na required to liberate 2240 ml hydrogen from water at N. T. P. *L. N. M.* U. *1974A.* Ans. 4·6 gms.

39. A mixture of KCl and NaCl was analysed and it was found that 0·654 gm of the mixture gave 1·465 gm AgCl. Find the percentage composition. *Bombay 1972* ; *Pat.* U. *1970.*

40. State the reaction of sodium carbonate with dilute hydrochloric acid, and with the help of a chemical equation, find the equivalent weight of sodium carbonate. [Na=23] *W. B. H. S. C. 1979.* Ans. 53.

41. (a) When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is (a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 9 : 4.

(b) 2·76 gm silver carbonate on being strongly heated yield a residue weighing (a) 2·16 gms (b) 2·48 gms (c) 2·32 gms (d) 2·64 gms. *I. I. T. 1979.* [$Ag_2CO_3 \rightarrow Ag_2O + CO_2$]

42. (a) How many molecules of hydrogen are liberated by the reaction of 1 gm of magnesium with excess of sulphuric acid ? (b) What is the volume of 1 gm of hydrogen at N. T. P. ? *W. B. H. S. C.* (*Vocational*) *1979.* Ans. $25{\cdot}095 \times 10^{21}$; 11·2 lits.

43. In the analysis of 0·500 g sample of feldspar, a mixture of the chlorides of sodium and potassium is obtained, which weighs 0·1180 g. Subsequent treatment of the mixed chlorides with silver nitrate gives 0·2451 g of silver chloride. What is the percentage of sodium oxide and potassium oxide in feldspar ? *I. I. T. 1979.* Ans. 0·434 ; 14·371.

44. Calculate moles of oxygen gas required for producing 400 g of magnesium oxide. [At. wt Mg=24] *W. B. J. E. E.* (*Tc*) *1979.* Ans. 5 moles.

45. A 2 gm sample containing Na_2CO_3 and $NaHCO_3$ loses 0·248 gm. When heated to 300°C, the temperature at which $NaHCO_3$ decomposes to Na_2CO_3, CO_2 and water. What is the percentage of Na_2CO_3 in the mixture ? *I. I. T. 1977.* Ans. 66·4%.

CHAPTER 8

Problems on Eudiometry (volume to volume calculations)

Eudiometry refers to only those chemical reactions in which gaseous reactants as well as products are involved in volume proportion under the same conditions of pressure and temperature (vide ; Gay Lussac's law). As for illustration, in the sulphur trioxide formation 1 volume of oxygen gas combines with 2 volumes of sulphur dioxide gas to yield 2 volumes of sulphur trioxide gas under the same conditions of temperature and pressure. The relation by volume amongst reactants and product is 1 : 2 : 2. Although according to Avogadro's hypothesis, gm molecular volume of all gases at S. T. P. is 22·4 litres, it is simply taken as volume for 22·4 litres. In solving problems a liquid or a solid is supposed to occupy negligible volume as compared with that of a gas, is considered.

The general procedure of calculations :

(i) Write a balanced equation for the relevant reaction ;

(ii) Write down volume or volumes beneath each of the reactants and products.

Some simple examples are given below to explain the facts mentioned so far.

(A) (i) $2H_2$ (gas) + O_2 (gas) = $2H_2O$ (steam) ;
2 volumes 1 volume 2 volumes

Contraction ; temp $\geqslant 100^\circ$C.
1 volume

Volume of oxygen = volume of contraction ; volumes of hydrogen and steam = twice the contraction.

(ii) $2H_2$ (g) + O_2 (g) = $2H_2O$ (l) ;

2 volumes 1 volume 0 volume

Conrtaction ; temp $< 100^\circ$C.
3 volumes

Volume of oxygen = $\frac{1}{3}$ rd of the contraction ; Volume of hydrogen = $\frac{2}{3}$ rd of the contraction.

['g' represents gaseous state and 'l' represents liquid state of a compound or an element)

(B) CO_2 (g) + C (S) = 2CO (g) ; expansion
1 volume 0 volume 2 volumes 1 volume

["S" represents solid state of a compound or an element]

(C) 2CO (g) + O_2 (g) = $2CO_2$ (g) ; Contraction
2 volumes 1 volume 2 volumes 1 volume

(D) C (S) + O_2 (g) = CO_2 (g) ; Contraction
0 volume 1 volume 1 volume 0 volume

(E) CH_4 (g) + $2O_2$ (g) = CO_2 (g) + $2H_2O$ (l) ;
1 volume 2 volumes 1 volume 0 volume
Contraction
2 volumes

(F) $2C_2H_2$ (g) + $5O_2$ (g) = $4CO_2$ (g) + $2H_2O$ (l) ;
2 volumes 5 volumes 4 volumes 0 volume
Contraction
3 volumes

(G) C_2H_4 (g) + $3O_2$ (g) = $2CO_2$ (g) + $2H_2O$ (l) ;
1 volume 3 volumes 2 volumes 0 volume
Contraction
2 volumes

(H) $C\ H_8$ (propane gas) + $5O_2$(g) = $3CO_2$ (g) + $4H_2O$(l) ;
1 volume 5 volumes 3 volumes 0 volume
Contraction
3 volumes

(I) N_2 (g) + O_2 (g) $\rightleftharpoons$ 2NO (g) ; Contraction
1 volume 1 volume 2 volumes 0 volume

(J) 2NO (g) + O_2 (g) = $2NO_2$ (g) ; Contraction
2 volumes 1 volume 2 volumes 1 volume

(K) N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g) ; Contraction
1 volume 3 volumes 2 volumes 2 volumes

(L) N_2O (g) + H_2 (g) = N_2 (g) + H_2O (l) ;
1 volume 1 volume 1 volume 0 volume
Contraction
1 volume

(M) $2Na\ (S) + 2HCl\ (g) = 2NaCl\ (S) + H_2\ (g)$
0 volume 2 volumes 0 volume 1 volume
Contraction
1 volume

(N) $2SO_3\ (g) \rightleftharpoons 2SO_2\ (g) + O_2\ (g)$; expansion
2 volume 2 volumes 1 volume 1 volume

In the gas analysis, different absorbents are used to remove gases e. g ; (i) Caustic potash for CO_2 and other acid gases ; (ii) alkaline pyrogallate for O_2 ; (iii) dilute H_2SO_4 for NH_3 ; (iv) ammoniacal cuprous chloride solution for CO and C_2H_2 (v) fuming H_2SO_4 for moisture, C_2H_4 etc.

Molecular formulae of gaseous hydrocarbons

Procedure : A known volume of the gaseous hydrocarbon is exploded with excess of oxygen. The immediate contraction on explosion and also the contraction on passing residual gas mixture through caustic patash are then noted down. Volume of CO_2 is known by 2nd contraction.

Experimental result and calculation :

1st method :

1st contraction = (volume of gases before explosion)—(volume of gases after explosion).

Or, 1st contraction = (volume of hydrocarbon + volume of excess of oxygen taken) − (volume of CO_2 produced + volume of oxygen remains unused).

Or, 1st contraction = volume of hydrocarbon + (volume excess of oxygen taken − volume of oxygen remains unused)—volume of CO_2 produced.

∴ 1st contraction = volume of hydrocarbon + volume of O_2 used up − volume of CO_2 produced (2nd contraction).

2nd method :

Let the molecular formula of hydrocarbon be C_xH_y. Where x and y represent the number of atoms of carbon and hydrogen respectively. The volume of hydrocarbon fired is supposed to be V_1 cc. First contraction $= V_2$ cc. 2nd contraction $=$ volume of CO_2 produced $= V_3$ cc.

The relevant equation is written below :

$$C_xH_y\ (g) + \left(x+\frac{y}{4}\right) O_2(g) = x\ CO_2(g) + \frac{y}{2}\ H_2O(l)\ ;$$

$$1 \text{ volume} \quad \left(x+\frac{y}{4}\right) \text{ volume } x \text{ volume O volume } \left(\frac{y}{4}+1\right) \text{ volume}$$

$$\text{contraction } V_1 \text{ cc} \left(x+\frac{y}{4}\right) \ V_1 \text{ cc } \ xV_1 \text{ cc } \ \text{O cc } \left(\frac{y}{4}+1\right) V_1 \text{ cc}$$

contraction.

[under the same conditions of pressure and temperature]

$$\text{1st contraction} = \left(\frac{y}{4}+1\right)V_1 \text{ cc} \quad \text{or, } V_2 \text{ cc} = \left(\frac{y}{4}+1\right)V_1 \text{ cc}$$

$$\text{or, } V_2 = \frac{y}{4}V_1 + V_1 \quad \text{or, } \frac{y}{4}V_1 = V_2 - V_1 \quad \text{or, } y = \frac{(V_2 - V_1)4}{V_1}.$$

$$\text{2nd contraction} = x\ V_1 \text{ cc} \quad \text{or, } V_3 \text{ cc} = x\ V_1 \text{ cc or, } x = \frac{V_3}{V_1}.$$

Knowing the values of V_1, V_2 and V_3 from experiments, molecular formula of a gaseous hydrocarbon (compound having contained carbon and hydrogen only) is easily determined.

Solved Problems :

1. 12 cc of a gaseous hydrocarbon are exploded with excess of oxygen. The contraction observed is 30 cc when treated with a solution of KOH there is a further contraction of 24 cc. What is the molecular formula of the hydrocarbon ?

West Bengal Joint Entrance E. 1969, '73, '74, '78, (Tech).

Let the molecular formula of hydrocarbon be C_xH_y. Where, x and y respresent the number of atoms of carbon and hydrogen respectively. Volume of hydrocarbon exploded $=12$ cc ; first contraction $=30$ cc ; 2nd contraction $=24$ cc.

$$y = \frac{(\text{volume of 1st contraction} - \text{volume of hydrocarbon exploded}) \times 4}{\text{volume of hydrocarbon exploded}}$$

$$\text{or, } y = \frac{(30-12)4}{12} = \frac{18 \times 4}{12} = 6.$$

$$x = \frac{\text{volume of 2nd contraction}}{\text{volume of hydrocarbon exploded}}$$

or, $x=\frac{24}{12}=2$. The molecular formula of the hydrocarbon is therefore C_2H_6.

2. What volume of oxygen gas at S.T.P. is necessary for complete combustion of 20 litres of propane (C_3H_8) measured at 27°C and 760 mm of Hg ? *I.I.T.* (Gp A) *1975.*

$$\text{We have, } \frac{P_0V_0}{T_0}=\frac{P_1V_1}{T_1} \quad \text{or, } \frac{1\times V_0}{273}=\frac{\frac{760}{760}\times 20}{273+27}$$

$$\text{or, } V_0=18{\cdot}2 \text{ litres.}$$

The relevant equation, $C_3H_8(g)+5O_2(g)\rightarrow 3\,CO_2(g)+4\,H_2O(l)$
1 volume 5 volumes (under the same conditions of temperature and pressure). ∴ volume of O_2 at S.T.P. required for complete combustion $=5\times 18{\cdot}2=91$ litres.

3. 0·9 gm of a solid organic compound (molecular weight 90) containing C, H and O, was heated with oxygen corresponding to a volume 224 ml at S.T.P. After combustion the total volume of the gases was 560 ml at S.T.P. On treatment with KOH, the volume decreased to 112 ml. Determine the molecular formula of the compound. *I.I.T. 1972.*

$$\text{We have, } C_xH_yO_z(S)+\left(\frac{y}{4}+x-\frac{z}{2}\right)O_2(g)\rightarrow xCO_2(g)+\frac{y}{2}H_2O(l)$$

$$1 \text{ gm mole } \left(\frac{y}{4}+x-\frac{z}{2}\right) 22400 \text{ ml } x.22400 \text{ ml O ml}$$

∵ 1 gm mole any gaseous substance occupies 22400 ml at S.T.P.

$$\therefore \frac{0{\cdot}9}{90}=0{\cdot}01 \text{ gm mole } \left(\frac{y}{4}+x-\frac{z}{2}\right) 22400.0{\cdot}01 \text{ ml } x.22400.0{\cdot}01\text{ml.}$$

Volume of CO_2 formed at S.T.P. $=560$ ml $-$ 112 ml $=448$ ml

∴ $x.22400.0{\cdot}01=448$ or, $x=2$.

Volume of O_2 used at S.T.P. $=224$ ml $-$ 112 ml $=112$ ml

$$\therefore \left(\frac{y}{4}+x-\frac{z}{2}\right) 22400.0{\cdot}01=112$$

$$\text{or, } \frac{y}{4}+x-\frac{z}{2}=\frac{112}{224}=\frac{1}{2} \quad \text{or, } \frac{y}{2}=z-3 \quad \because \; x=2.$$

Now, according to law of conservation of mass,

$$90+\left(\frac{y}{4}+x-\frac{z}{2}\right)32=44x+\frac{y}{2}18$$

Or, $90+\left(\frac{y}{2}\cdot\frac{1}{2}+2-\frac{z}{2}\right)32=44.2+\frac{y}{2}.18$

Or, $90+\frac{y}{2}\cdot\frac{1}{2}\cdot 32+2.32-\frac{z}{2}\cdot 32=88+\frac{y}{2}\cdot 18$

Or, $90+(z-3)\frac{1}{2}.32+64-z.16=88+(z-3)\,18 \quad \because \quad \frac{y}{2}=z-3.$

Or, $90+16z-48+64-16z=88+18z-54$

Or, $106=34+18z$ Or, $18z=72 \quad \therefore \quad z=4.$

$\because \quad \frac{y}{2}=z-3$ Or, $^{y}=4-3=1 \quad \therefore \quad y=2.$

Molecular formula of the solid organic compound is therefore $C_2H_2O_4$.

4. 25 ml. of oxygen are subjected to silent electric discharge and the volume of ozonised oxygen becomes 20 ml. What is the composition of the ozonised oxygen ?

Volume of O_3 is supposed to be x ml. Volume of O_2 in the mixture is therefore $(20-x)$ ml. We have, $3O_2 \rightleftharpoons 2O_3$. According to the equation, 2 ml. O_3 produce 3 ml. O_2 under the same conditions of temperature and pressure. Therefore, x ml O_3 produce $\frac{3}{2}x$ ml O_2. So, volume of oxygen unused + volume of oxygen used in to form ozone $=(20-x)$ ml $+\frac{3}{2}x$ ml. $\therefore$ by the question $(20-x)$ ml $+\frac{3}{2}x$ ml $=25$ ml or, $x=10$ ml. Volume of ozone $=10$ ml ; volume of oxygen $=(20-10)$ ml $=10$ ml.

5. 100 cc of a mixture of nitrous and nitricoxide are slowly passed over red-hot copper. The resulting gas occupied a volume of 85 cc both measured under the same conditions of temperature and pressure ; 20 cc of oxygen were added to another 100 cc of the same mixture and the volume contracted in this case from 120 cc to 105 cc. Assuming that NO is converted to NO_2, find the composition of this 105 cc of gas mixture.

Calcutta U. *B. Sc. 1973.*

Volume of NO is supposed to be x cc. Volume of N_2O is therefore, $(100-x)$ cc. We have the equations:

(a) $\underset{x\text{ cc}}{NO(g)}+Cu(s)=CuO(s)+\underset{\frac{x}{2}\text{ cc}}{\tfrac{1}{2}N_2(g)}$;

(b) $\underset{(100-x)\text{cc}}{N_2O(g)}+Cu(s)=CuO(s)+\underset{(100-x)\text{cc}}{N_2(g)}$

$\therefore$ total volume of nitrogen produced $=\frac{x}{2}\text{cc}+(100-x)\text{cc}$.

According to the question, $\frac{x}{2}\text{ cc}+(100-x)\text{cc}=85\text{ cc}$

$\therefore\ x=30$ cc.

100 cc mixture contain 30 cc NO and 70 cc N_2O.

In the second case we have, $2NO(g)+O_2(g)=2NO_2(g)$.

30 cc NO combine with 15cc O_2 to form 30cc NO_2. Volume of unused $O_2=20\text{ cc}-15\text{ cc}=5\text{ cc}$; Volume of $NO_2=30$ cc and volume of $N_2O=70$ cc.

6. Nitric oxide alone does not explode with hydrogen but does so when mixed with an equal volume of nitrous oxide. 20 cc of each of these oxides mixed with 40 cc of hydrogen were exploded. All the hydrogen was used up and 30 cc of nitrogen produced. Find the molecular formula of nitric oxide, if that of nitrous oxide be N_2O.

We have, $N_2O(g)+H_2(g)=H_2O(l)+N_2(g)$.

$\therefore$ 20 cc N_2O on reacting with 20 cc H_2 yield 20 cc N_2.

$\therefore$ N_2 formed from nitric oxide $=(30-20)\text{cc}=10$ cc.

$\because$ total volume of nitrogen produced $=30$ cc. Volume of H_2 used by nitric oxide $=(40-20)\text{ cc}=20$ cc. As 20 cc H_2 react with 10 cc O_2, 20 cc nitric oxide contain 10 cc O_2 and 10 cc N_2 under the same conditions of temperature and pressure. $\therefore$ 1 cc nitric oxide contains $\frac{1}{2}$ cc O_2 and $\frac{1}{2}$ cc N_2. Or, 1 mole nitric oxide contains $\frac{1}{2}$ mole O_2 and $\frac{1}{2}$ mole N_2. $\because$ Oxygen and nitrogen are diatomic molecule. $\therefore$ formula of nitric oxide is NO.

7. 25 cc of marsh gas at S.T.P. are mixed up with 300 cc air at 300°K and 75 cm pressure and the mixture is fired by electric sparks, Find out the volume of the residual gas at S.T.P. Air contains 20% oxygen and 80% nitrogen by volume at S.T.P.

We have, $\frac{P_0V_0}{T_0}=\frac{P_1V_1}{T_1}$; $\frac{76V_0}{273}=\frac{75\times 300}{300}$; where $V_0=269{\cdot}4$cc = Volume of air at S.T.P. 269·4 cc of air contain therefore, $\frac{20\times 269{\cdot}4}{100}=53{\cdot}88$ cc O_2 and $\frac{80\times 269{\cdot}4}{100}=215{\cdot}52$ cc N_2 at S.T.P.

Combustion of marsh gas is represented by the equation, $CH_4(g)+2O_2(g)=2H_2O(l)+CO_2(g)$. ∴ 25 cc marsh gas at S.T.P. react with 50 cc O_2 and produce 25 cc CO_2. Volume of O_2 remains unreacted = (53·88 − 50) cc = 3·88 cc.

∴ the volume of the residual gas mixture = 215·52 cc N_2 + 3·88 cc O_2 + 25 cc CO_2 = 244·4 cc at S.T.P.

8. When 10 cc of a mixture of oxygen and nitrogen are mixed with 20 cc of hydrogen and exploded, then 21 cc of a gas are left. Find out the percentage composition of the given mixture.

Ranchi U. *1968, '71.*

Volume of the mixture containing oxygen and nitrogen = 10 cc ;

Volume of the mixture after addition of hydrogen = 30 cc ;

Volume of the mixture after explosion = 21 cc. ∴ Contraction in volume = (30 − 21) cc = 9 cc. This contraction is considered only due to the formation of liquid water according to the following equation ; $\underset{\text{2 vols}}{2H_2(g)}+\underset{\text{1 vol}}{O_2(g)}\rightarrow\underset{\text{0 vol}}{2H_2O(l)}$.

We have now known $\frac{1}{3}$rd of the total contraction is the volume of oxygen used. Of course, possibility of occurring reaction of nitrogen with either hydrogen or oxygen is remote.

∴ Volume of oxygen in the mixture $=\frac{1}{3}\times 9=3$ cc ; volume of nitrogen = (10 − 3) cc = 7 cc ; % of $O_2=\frac{3}{10}\times 100=30$; % of $N_2=\frac{7\times 100}{10}=70$.

9. If excess of phosphorous is fired in 20 cc nitrous oxide, what volume of nitrogen will be produced under the conditions

of same temperature and pressure? If nitric oxide (20 cc) is utelised in lieu of nitrous oxide in the aforesaid experiment, what volume of nitrogen will be obtained?

$$2P(s)+5N_2O(g)\rightarrow P_2O_5(s)+5N_2(g)\ ;$$
$$20\text{ cc} \qquad\qquad 20\text{ cc}$$

$$2P(s)+5NO(g)\rightarrow P_2O_5(s)+\tfrac{5}{2}N_2(g)$$
$$20\text{ cc} \qquad\qquad \tfrac{20}{2}\text{ cc}$$

Volume of nitrogen produced in the 1st case = 20 cc; in the 2nd case = 10 cc.

10. A mixture of 20 cc of hydrogen and 10 cc of chlorine is allowed to expose over diffused sunlight until completion of the reaction. Find the volume of the mixture after the reaction is over. If the vessel containing resulting mixture is left exposed to mercury and water separately. What volume of the liquids will rush in?

$$H_2(g)+Cl_2(g)\rightarrow 2HCl(g)\ ;$$
$$10\text{cc} \quad 10\text{cc} \quad 20\text{cc}$$

Volume of the mixture after reaction = 20 cc HCl + 10 cc H_2 = 30 cc. 0 cc Hg(l) and 20 cc $H_2O(l)$ rush in because this volume of HCl dissolves in water.

11. 50 cc ammonia is reacted with 15 cc chlorine. What will be the volume of the gas mixture after completion of the reaction? The resulting mixture is finally shaken with excess of dil H_2SO_4. Find out the volume of the residual gas after absorption.

$$8\ NH_3(g)+3\ Cl_2(g)=N_2(g)+6NH_4Cl(s)\ ;$$
$$40\text{ cc} \quad 15\text{ cc} \quad 5\text{ cc} \quad 0\text{ cc}$$

Volume of the gas mixture after reaction

$$=(50-40)\text{ cc }NH_3+5\text{ cc }N_2=15\text{ cc.}$$

$$2NH_3(g)+H_2SO_4^{=}(l)=(NH_4)_2SO_4(s)\ ;$$
$$10\text{ cc} \quad 0\text{ cc} \quad 0\text{ cc}$$

Volume of the residual gas after obsorption = 5 cc N_2.

∵ 10 cc NH_3 get absorbed by dil H_2SO_4.

12. A 40 ml sample of a mixture of H_2 and O_2 was placed in a gas burette at 18°C and 1 atm pressure. A spark was applied so that the formation of water was complete. The remaining pure gas had a volume of 10 ml at 18°C and 1 atm. If the remaining gas was H_2, what was the initial mole percent of H_2 in the mixture ? *I.I.T. 1976.*

We have, $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ contraction
2 volume 1 volume 0 volume 3 volume
under same temp. and pr.

Contraction in volume because of explosion $= (40-10)$ ml $= 30$ ml.

According to the above equation, $\frac{1}{3}$rd. contraction = volume oxygen used $= \frac{1}{3} \times 30$ ml $= 10$ ml ; $\frac{2}{3}$rd contraction = volume of hydrogen used $= \frac{2}{3} \times 30$ ml $= 20$ ml. $\therefore$ 40 ml initial mixture contain $(20+10)$ ml H_2 and 10 ml O_2. Initial mole percent of H_2 in the gas mixture is therefore $\frac{30 \times 100}{40} = 75$.

13. 60 ml of a mixture of equal volume of chlorine and an oxide of chlorine was heated and then cooled back to the original temperature. The resulting gas mixture was found to have a volume of 75 ml. On treatment with NaOH solution the volume contracted to 15 ml. Assuming that all measurements were made at the same temperature and pressure, deduce the simplest formula of the oxide of chlorine. *I. I. T. 1971.*

Molecular formula of the oxide of chlorine is supposed to be Cl_mO_n. Before heating volume of Cl_2 and Cl_mO_n is 30 ml separately. Contraction in volume $= (75-15)$ ml $= 60$ ml $=$ total volume of Cl_2 reacted with NaOH soln. Volume of Cl_2 produced $= (60-30)$ ml $= 30$ ml. Residual volume of the gas after treatment with NaOH soln $= 15$ ml $=$ volume of oxygen evolved. As, $Cl_mO_n = \frac{m}{2} Cl_2 + \frac{n}{2} O_2$, 30 ml $Cl_mO_n(g)$ yield 30 ml $Cl_2(g)$ and 15 ml $O_2(g)$ i.e., 1 ml $Cl_mO_n(g)$ yields 1 ml $Cl_2(g)$ and $\frac{1}{2}$ ml $O_2(g)$, $\therefore$ $\frac{m}{2} = 1$ or, $m = 2$; $\frac{n}{2} = \frac{1}{2}$ or, $n = 1$.

Molecular formula of the oxide of chlorine is therefore Cl_2O.

14. Nine volumes of a gaseous mixture consisting of a gaseous organic compound A, and just sufficient amount of oxygen required for complete combustion yielded on burning 4 volumes of CO_2, 6 volumes of water vapour and 2 volumes of N_2, all volumes measured at the same temperature and pressure. If the compound A contained only carbon, hydrogen and nitrogen :— (i) How many volumes of oxygen are required for complete combustion ? (ii) What is the molecular formula of the compound A ? *I. I. T. (Group A) 1974.*

Formula of the gaseous organic compound A is supposed to be $C_xH_yN_z$.

We have now, $C_xH_yN_z + \left(x+\frac{y}{4}\right)O_2 \rightarrow xCO_2(g) + \frac{y}{2}H_2O(g) + \frac{z}{2}N_2(g)$

1 volume $\left(x+\frac{y}{4}\right)$ volumes x volumes $\frac{y}{2}$ volume $\frac{z}{2}$ volume

V volumes $(9-V)$ volumes 4 volumes 6 volumes 2 volumes

or, V volumes $\left(x+\frac{y}{4}\right)$ V volumes Vx volumes $\frac{y}{2}$ V volumes $\frac{z}{2}$ V volumes

$\therefore\ Vx=4\cdots$(i) ; $\frac{yV}{2}=6\cdots$(ii) ; $\frac{zV}{2}=2\cdots$(iii).

Dividing (i) by (ii) we get $y=3x\cdots$(iv). Dividing (i) by (iii) we get $x=z\cdots$(v).

Again, $\left(x+\frac{y}{4}\right)V=9-V$ or, $V\left(\frac{4x+y}{4}+1\right)=9\cdots$(vi).

Dividing (i) by (vi) we get $y+4=5x\cdots$(vii). Solving (iv), (v) and (vii) we get $V=2$; $x=2$; $y=6$; $z=2$. (i) volume of oxygen used is therefore $9-2=7$ and (ii) molecular formula of A is $C_2H_6N_2$.

15. One litre of mixture of CO and CO_2 is found to give 1600 cc of CO on being passed through a tube containing red-

hot charcoal both measured under the same conditions, calculate the composition of the mixture. *West Bengal Joint Entrance 1970.*

Let the volume of CO = X cc.

∴ Volume of CO_2 in the mixture = $(1000 - X)$ cc.

According to the equation, $CO_2(g) + C(s) = 2CO(g)$;

$2(1000 - X)$ cc CO is formed.

∴ X cc + $2(1000 - X)$ cc = 1600 cc or, $X = 400$ cc.

So, 1 litre mixture contains 400 cc CO and (1000 − 400) cc = 600 cc CO_2.

16. What volume of oxygen would be required to burn completely a mixture of 40 ml of hydrogen sulphide and 60 ml of methane? *Bombay* U. *1976.*

$$\underset{40\text{ ml}}{2H_2S(g)} + \underset{20\text{ ml}}{O_2(g)} \rightarrow 2H_2O + 2S \;;$$

$$\underset{60\text{ ml}}{CH_4(g)} + \underset{120\text{ ml}}{2O_2(g)} \rightarrow CO_2(g) + 2H_2O$$

Volume of oxygen required for complete combustion = 20 ml + 120 ml = 140 ml.

17. Ethylene is mixed with just sufficient nitrous oxide for complete reaction and exploded. If the volume of the gaseous product is 80 cc, find the volumes of ethylene and nitrous oxide under the same condition of pressure and temperature.

We have, $\underset{1\text{ volume}}{C_2H_4(g)} + \underset{6\text{ volumes}}{6N_2O(g)} = \underset{2\text{ volumes}}{2CO_2(g)} + \underset{0\text{ volume}}{2H_2O(l)} + \underset{6\text{ volumes}}{6N_2(g)}$

According to the equation, 2 volume CO_2 and 6 volume N_2 are produced. Volume of CO_2 is $\frac{1}{4}$th of the total volume of the liberated gas mixture. ∴ Volume of CO_2 formed = $\frac{80}{4}$ cc = 20 cc.

As 2 volume CO_2 have come from 1 volume C_2H_4 ; volume of $C_2H_4 = \frac{20}{2}$ cc. = 10 cc. Again, 1 volume C_2H_4 combines with 6 volume N_2O. ∴ Volume of $N_2O = 10 \times 6$ cc = 60 cc.

18. On passing electric spark through 10 cc ammonia taken in an eudiometer tube the volume increased to 20 cc. The resulting gas was exploded with 30 cc oxygen and on cooling the

volume was 27·5 cc. All volumes were measured under similar conditions of temperature and pressure. Vapour density of ammonia is 8·5. Calculate its molecular formula.

Rajasthan U. 1963.

Let the molecular formula of ammonia be N_xH_y assuming that ammonia contains only nitrogen and hydrogen. Where, x = number of atoms of nitrogen and y = number of atoms of hydrogen.

We have, $N_xH_y \rightleftharpoons \frac{x}{2}N_2 + \frac{y}{2}H_2$; $\frac{y}{2}H_2 + \frac{y}{4}O_2 \rightarrow \frac{y}{2}H_2O$

10 cc 5x cc 5y cc 5y cc $\frac{5}{2}y$ cc

$\therefore$ expansion in volume $= (20-10)$ cc $= (5x+5y-10)$ cc

or, $10 = 5x+5y-10$ or, $x+y=4 \cdots$(i)

5x cc N_2 + unused $O_2 = 27{\cdot}5$ cc

or, unused $O_2 = (27{\cdot}5 - 5x)$ cc.

Total volume of O_2 taken = 30 cc

$\therefore$ used $O_2 = (30 - 27{\cdot}5 + 5x)$ cc

or, $\frac{5}{2}y = 2{\cdot}5 + 5x$ or, $2x - y = -1 \cdots$(ii)

Solving (i) and (ii) we get $x=1$; $y=3$.

Molecular formula of ammonia is therefore NH_3. This is further confirmed by the given vapour density of ammonia.

$\because$ 2X vapour density = mol. wt = 2X 8·5 = 17 ; at wt of nitrogen = 14 and at wt of hydrogen = 1.

19. 20 cc of a gas containing only hydrogen and sulphur is heated with tin. When the reaction was over, there was no change in volume. Residual gas was hydrogen. If the molecular weight of the gas is 34, calculate its molecular formula.

Rajasthan U. 1967.

Let the molecular formula of the gas be H_xS_y. Where, x = number of atoms of hydrogen and y = number of atoms of sulphur.

We have, $H_xS_y(g) + \frac{y}{2}\,Sn(s) \rightarrow \frac{y}{2}\,SnS_2(s) + \frac{x}{2}\,H_2(g)$

20 cc 10x cc

$\therefore$ $(10x - 20)$ cc $= 0$ cc.

$\because$ change in volume becomes nil according to the question.

or, $x=2$. Now, $34=1.x+32.y$ $\therefore$ $y=1$. Formula is H_2S.

20. 50 cc of a gaseous mixture of H_2 and HCl was exposed to sodium amalgam. The volume decreased to 42·5 cc. If 100 cc of the same mixture is mixed with 50 cc of gaseous ammonia and then exposed to water, what will be the final volume ?

(All the volumes are measured at the same temperature and pressure) *I. I. T. 1972*

Let the volume of hydrogen chloride gas (HCl) in the mixture become x cc. Volume of hydrogen in the mixture is therefore $(50-x)$ cc. Hydrogen chloride combines with sodium amalgam following the equation, $2Na(s)+2HCl(g)=2NaCl(s)+H_2(g)$.

According to the equation, x cc HCl yields $\frac{x}{2}$ cc H_2.

So, total volume of hydrogen after reaction $=\left(50-x+\frac{x}{2}\right)$cc.

By the question, $\left(50-x+\frac{x}{2}\right)$ cc $=$ 42·5 cc $\therefore$ $x=15$ cc.

Now, 50 cc original gaseous mixture contain 15 cc HCl

$\therefore$ 100 cc ” ” ” ” 30 cc ” .

This “30 cc HCl” combines with 30 cc NH_3 to form ammonium chloride. So, 20 cc of ammonia remain unused. 20 cc ammonia dissolve in water. $\therefore$ the residual gas mixture contain only hydrogen, volume of which is $(50-15)2$ cc $=70$ cc.

or, $(100-30)$ cc $=70$ cc.

21. A sample of coal gas contained 45%H, 30%CH_4, 20%CO and 5% C_2H_2. 100 cc of it were mixed with 160 cc of O_2 and exploded. Calculate the volume and composition of the resulting mixture (all being dry gases). *Ranchi* U. 1973.

$2H_2(g)+O_2(g)\rightarrow 2H_2O(g)$; $CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(g)$

45 cc 22·5 cc 45 cc 30 cc 60 cc 30 cc 60 cc

$2CO(g)+O_2(g)\rightarrow 2CO_2(g)$; $2C_2H_2(g)+5O_2(g)\rightarrow 4CO_2(g)+2H_2O(g)$

20 cc 10 cc 20 cc 5 cc 12·5 cc 10 cc 5 cc

Volume of oxygen used = 22·5 cc + 60 cc + 10 cc + 12·5 cc = 105 cc ; volume of oxygen taken = 160 cc ; volume of oxygen unused = (160 − 105) cc = 55 cc ; volume of water vapour = 45 cc + 60 cc + 5 cc = 110 cc and volume of CO_2 = 30cc + 20 cc + 10 cc = 60 cc.

Problems for practice :

1. 50 cc of a mixture of CO, CO_2, H_2 and 20 cc of O_2 at R. T. P. were exploded. The volume after explosion measured at the original R. T. P. was 37 cc and after treatment with KOH, volume was 3 cc. Calculate the composition of original mixture by volume. *Ranchi* U. *Pre.* U. *1966.* Ans. 18 cc CO ; 16 cc CO_2 ; 16 cc H_2.

2. A mixture of marsh gas (methane) and acetylene require 22 cc of oxygen for complete combustion and yield 14 cc CO_2. Find the volume of marsh gas and acetylene. Ans. 6 cc marsh gas ; 4 cc acetylene.

3. 20 cc of a mixture of CO, CH_4 and N_2 exploded with excess of oxygen, gave a contraction of 13 cc ; there was a further contraction of 14 cc when the residual gas was treated with KOH. What was the composition of the gas mixture ? Ans. vol of CH_4 = 4 cc ; vol of CO = 10 cc ; vol of N_2 = 6 cc.
Bihar U. *1960* ; *Ranchi U. 1969.*

4. 30 cc of a mixture of CO and C_2H_2 were mixed with 50 cc of O_2 in an eudiometer tube and fired. After cooling, the residual gases occupied 55 cc and after treatment with potash, the residual oxygen occupied 15 cc. What was the volumetric composition of the mixture ? Volumes were measured at N.T.P.
Ranchi U. *1963.* Ans. 66·6% CO ; 33·4% C_2H_2.

5. 100 cc of an oxide of nitrogen yield 50 cc of nitrogen under the same conditions of pressure and temperature. The molecular weight of the oxide at R.T.P. is 46. What is its molecular formula ? Ans. NO_2.

6. 15 cc of a mixture of hydrogen and acetylene required 19·5 cc of oxygen for complete combustion. Calculate the percentage composition of the mixture by volume.

Punjab U. *I. Sc. Supp. 1966.* Ans. 60% H_2 ; 40% C_2H_2.

7. When 60 cc of a mixture of nitrous oxide and nitric oxide were mixed with equal volume of pure hydrogen and exploded, 38 cc of pure nitrogen were left. Calculate the volumetric composition of the original mixture. Ans. 16 cc N_2O ; 44 cc NO.

Ranchi U. *1965S.*

8. 40 cc of H_2S are exploded with 100 cc of oxygen. (ii) If all the volumes, before and after, are measured at N. T. P. ; what is the volume composition of the resulting mixture ? (ii) If all volumes are measured at 200°C and normal pressure, what is the volume composition of the resulting mixture ?

Senior Cambridge 1966. Ans. (i) $SO_2=40$ cc ; $O_2=40$ cc (ii) 40 cc SO_2 ; 40 cc O_2 ; 40 cc steam.

9. Calculate the percentage composition by volume of a mixture of CO and CH_4, 10·5 cc of which requires 2 cc of oxygen for complete combustion. *Punjab* U. *I.Sc. 1966.* Ans. 76·19%CO ; 23·81%CH_4.

10. One volume of gaseous compound containing carbon, hydrogen and oxygen was burnt in the presence of 2·5 volumes of oxygen. On complete combustion the resultant gases contained 2 volumes of steam and 2 volumes of carbon dioxide. All volumes were measured under identical conditions. What is the formula of the compound ? *I.I.T. 1966.* Ans. C_2H_4O.

11. A sample of gas was found to contain hydrogen, methane and carbon monoxide, 30 cc of this mixture was exploded in an eudiometer tube with 120 cc of oxygen. On cooling the resulting gas was found to be 102 cc. Absorption by caustic potash further reduced the volume by 15 cc. Calculate the percentage of the constituents in the mixture. *Punjab Joint Entrance 1966.* Ans. 50%H_2 ; 40%CH_4 ; 10%CO.

12. 12 cc of a hydrocarbon were mixed with excess of oxygen in an eudiometer tube and exploded. There was a contraction of 30 cc in volume of the gas mixture. On adding caustic potash solution there was a further contraction of 24 cc. All volumes were measured on dry gas basis at 25°C and under 760 mm pressure. What is the formula of the hydrocarbon ? *Calcutta* U. *B. Sc.* 1967. Ans. C_2H_6.

13. 24 ml of water gas, containing only hydrogen and carbon monoxide in equal proportions by volume, are exploded with 80 ml of air, 20% by volume of which is oxygen. If all gaseous volumes are measured at room temperature and pressure, calculate the composition by volume of the resulting gaseous mixture ? *Senior Cambridge 1967.* Ans. 64 ml N_2 ; 4 ml O_2 ; 12 ml CO_2.

14. 20 cc of gaseous hydrocarbon was exploded with excess of oxygen in an eudiometer tube. On cooling, the volume of resultant gases was reduced by 50 cc. On further treatment with KOH soln there was a further contraction of 40 cc. Calculate the molecular formula of the hydrocarbon.

Punjab Joint Entrance 1967. Ans. C_2H_6.

15. One litre of nitric Oxide at N. T. P. weighs 1·339 gm. One volume of nitrogen combines with one volume of oxygen forming two volumes of nitric oxide. Find the molecular formula of nitric oxide. *Ranchi* U. *Pre.* U. 1968S. Ans. NO.

16. 20 cc of a gaseous hydrocarbon are exploded with excess of O_2. The contraction observed is 30 cc. When treated with a solution of KOH, there is a further contraction of 40 cc. What is the formula of the gas ? *Ranchi* U. *1970.* Ans. C_2H_2.

17. 100 cc of a mixture of carbon monoxide, methane and hydrogen when mixed with 300 cc of oxygen and fired. After cooling, the resulting gases occupied 285 cc and after absorption by potash 205 cc of oxygen remained. Determine the composition of the mixture. All the gases were measured under same temperature and pressure. *West Bengal Joint Entrance 1971.*

Ans. 20 cc H_2 ; 50 cc CO_2 and 30 cc CH_4.

18. 10 cc of a gaseous hydrocarbon is exploded with an excess of O_2, when there is a contraction of 20 cc. On absorption with KOH, there is a further contraction of 20 cc. Find the molecular formula of the hydrocarbon. *Ranchi* U. *I. Sc. 1972S.* Ans. C_2H_4.

19. 500 cc of a hydrocarbon gas burnt in excess oxygen yields 2500 cc of carbon dioxide and 3 litres of water vapour, all the volumes being measured at the same temperature and presure. What is the formula of the hydrocarbon gas ?

I. I. T. (Gp. B) 1974. Ans. C_5H_{12}.

20. 10 cc of carbon monoxide are exploded with 20 cc of oxygen in an eudiometer over mercury. What volume of the gas is left and what is its composition ? *Ranchi* U. *1974S.*

Ans. 25 cc ; 10 cc CO_2 ; 15 cc unused O_2.

21. 32 cc of a mixture of carbon monoxide, methane and hydrogen were mixed with 50 cc oxygen and exploded. After cooling to room temperature, the volume was noted. The volume was reduced by 22 cc, when exposed to potassium hydroxide solution, leaving 16 cc of excess oxygen. Calculate the composition of the mixture. *West Bengal Joint Entrance 1975.*

Ans. 12 cc CH_4 ; 10 cc CO ; 10 cc H_2.

22. Ten ml of a gaseous hydrocarbon was burnt completely in 80 ml of O_2 at N. T. P. The remaining gas occupied 70 ml at N. T. P. This volume became 50 ml on treatment with KOH solution. What is the empirical formula of the hydrocarbon ?

I. I. T. (Gp. A) 1976. Ans C_2H_4.

23. 20 cc of a gaseous hydrocarbon were exploded with 66 cc of oxygen. Residual gases after cooling occupied 56 cc. On treatment with KOH the volume decreased to 16 cc. The remaining gas was oxygen only. What is the molecular formula of the hydrocarbon ?

West Bengal Joint Entrance 1976. Ans. C_2H_2.

24. A certain volume of a gaseous mixture of CO and CH_4 was mixed with 5 ml of H_2 and excess of O_2 in an eudiometer and exploded. The contraction in volume was found to be 26 ml. It was then treated with KOH soln and a further contraction of 11·5 ml was observed. Volumes of properly dried gases at each stage was measured at N. T. P. Calculate the composition of the given gaseous mixture. *Calcutta* U. *B. Sc.* 1977 Ans. 3 ml CO ; 8·5 ml CH_4.

25. 24 cc of a mixture of methane and ethane were exploded with 90 cc of oxygen. After cooling to room temperature, the volume of gas was noted. It was found to decrease by 32 cc when treated with caustic potash solution. Calculate the camposition of the mixture. *W. B. J. E. E. 1977* Ans. $CH_4 =$ 16 cc ; $C_2H_6 = 8$ cc.

26. 100 ml of water gas $(CO+H_2)$ containing some carbon-dioxide was exploded with 100 ml of oxygen and the volume after explosion was 100 ml. On introducing sodium hydroxide the volume was reduced to 52·5 ml. State the reactions involved and find out the percentage composition of the mixture.

Patna U. 1969 A. Ans 42·5 ml CO ; 52·5 ml H_2 ; 5 ml CO_2.

27. 40 cc of a mixture of hydrogen, methane and nitrogen was exploded with 10 cc of oxygen. After cooling, the residual gas measured 36·5 cc. On treatment with caustic potash, the volume diminished to 33·5 cc and on treatment with alkaline pyrogallol to 32 cc. Calculate the percentage composition of the original mixture. *Ranchi* U. ; *Magad* U. *1967*. Ans. 12·5%H_2 ; 7·5%CH_4 ; 80%N_2.

28. 10 cc of a hydrocarbon was mixed with 70 cc of oxygen and the mixture, sparked. The volume after explosion was 55 cc and this was reduced to 35 cc by treatment with caustic potash solution, all volumes being measured at the same temperature and pressure. Deduce the molecular formula of the gas.

Ranchi U. *1964 A* ; *1974 A*. Ans C_2H_6.

29. A sample of coal gas has the following composition: hydrogen = 50%, methane = 35%, nitrogen = 2%, ethylene = 5%, carbon monoxide = 8%. Calculate the volume of air required for the combustion of 1 litre of this mixture, assuming that air contains 20% of oxygen by volume and all the gases have been measured under the same condition of temperature and pressure.
Patna U. *1970A*. Ans. 5·8 litres.

30. 9 ml of oxygen is required for complete combustion of 10·5 ml of a mixture of carbon monoxide and methane. Calculate the percentage by volume of each in the original mixture.
Bhagalpur U. *1975S*. Ans. 76·19%CO ; 23·81% CH_4.

31. When 15 cc of a mixture of oxygen and nitrogen mixed with 30 ml of hydrogen at 25°C and exploded, 27 ml of gas is left on cooling to 25°C. Find out the percentage composition of mixture. *Ranchi* U. *1975A*. Ans. 40%O_2 ; 60%N_2.

32. 5 cc of a hydrocarbon gas are exploded with an excess of oxygen. The contraction in volume is found to be 10 cc. It is then treated with KOH soln and a further contraction of 10 cc is observed. Deduce the molecular formula of the hydrocarbon.
Ranchi U. *1972* ; *L.N.M.*U. *1975A*. Ans. C_2H_4.

33. 60 cc of a mixture of CO and H_2 yielded 20 cc of CO_2 after explosion with excess of O_2. What is the percentage of CO in the mixture. *Patna* U. *1973*. Ans. 33·33.

34. 15 cc of NH_3 are completely decomposed by eletric sparks in an eudiometer tube, 40 cc of O_2 added and the mixed gases exploded. State the gases present before and after explosion and determine composition in volume. *Mag.* U. *1975*. Ans. N_2, H_2, O_2 ; N_2, O_2 ; 7·5 cc, 22·5 cc ; 7·5 cc, 28·75 cc.

35. Establish the formula of marsh gas from the given data: Vol of gas taken = 10 cc ; Vol of O_2 added = 25 cc ; Vol after explosion = 15 cc and vol. after NaOH treatment = 5 cc.
Cuttack '71, CH_4.

36. 40 cc of H_2 is added to a mixture of 20 cc each of nitric and nitrous oxide are exploded. The residual volume which is 30 cc, contains only nitrogen. Find out the formula for nitric oxide if that of nitrous oxide is N_2O. *Ranchi* U. *1978*. Ans. NO.

37. 20 ml of a gaseous hydrocarbon was exploded with oxygen avoiding excess. On cooling, the volume was found to be 60 ml. The vapour density of the hydrocarbon is 22. Find the molecular formula of the hydrocarbon.

W. B. J. E. E. (Tc). 1979.

[Hint. $20X=60$; $X=3=$no of atoms of carbon. $12X+Y=22\times2$ $\therefore$ $Y=8$. Formula of C_xH_y is C_3H_8.]

38. 5 ml of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 ml) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 ml. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 ml, the residual gas being pure oxygen. All volumes have been reduced to N. T. P. Calculate the molecular formula of the hydrocarbon gas. *I. I. T. 1979*. Ans. C_2H_4.

39. Ten ml. of a gaseous organic compound containing C, H and O only, was mixed with 100 ml of O_2 and exploded under conditions which allowed the water formed to condense. The volume of the gas after explosion was 90 ml. On treatment with potash solution a further contraction in volume of 20 ml was observed. Given that the vapour density of the compound is 23, deduce the molecular formula. All volume measurements were carried out under the same conditions.

I. I. T. 1977. Ans. C_2H_6O.

40. A sample of gaseous hydrocarbon occupying 1·12 litres at N. T. P., when completely burnt in air produced 2·2g of CO_2 and 1·8g of H_2O. Calculate the weight of the compound taken and the volume of O_2 at N. T. P. required for its burning. Find the molecular formula of the hydrocarbon. *I. I. T. 1978.*

[Hints. $C_xH_y + \left(x+\frac{y}{4}\right)O_2 = xCO_2 + \frac{y}{2}H_2O$. Vol. of 2·2 g of $CO_2 = \frac{22{\cdot}4 \times 2{\cdot}2}{44} = 1{\cdot}12$ lit. at N. T. P. Vol. of 18 g of $H_2O = \frac{22{\cdot}4 \times 1{\cdot}8}{18} = 2{\cdot}24$ lit. at N. T. P.

Vol. of $CO_2 = 1{\cdot}12x = 1{\cdot}12$ $\therefore$ $x = 1$. Vol. of $H_2O = 1{\cdot}12\frac{y}{2} = 2{\cdot}24$; $y = 4$.

Formula is CH_4. Vol. of O_2 used $= 1{\cdot}12\left(x+\frac{y}{4}\right) = 2{\cdot}24$ lit. at N. T. P. Wt. of 1·12 litres of CH_4 at N. T. P. $= \frac{16 \times 1{\cdot}12}{22{\cdot}4} = 0{\cdot}8$g.]

41. 12 ml of a gaseous hydrocarbon were mixed with 50 ml of oxygen in an eudiometer tube and exploded. After explosion and cooling the volume of the gas (mixture) was found to be 32 ml. On adding KOH there was a further contraction of volume by 24 ml. Find out the molecular formula of the gas.

Ravisankar U. 1978 (B. Sc.). Ans. C_2H_6.

42. 20 cc of a gaseous hydrocarbon was mixed with 80cc of a oxygen, and the mixture exploded. After explosion the volume was 60cc. The addition of KOH further reduced the volume to 40cc. Find the molecular formula of the hydrocarbon.

Ravisankar U. 1973 (B. Sc.). Ans. CH_4.

43. 30cc of a gaseous hydrocarbon was burnt in an excess of O_2. After cooling the total volume, a contraction of 60 cc was observed. On treatment with KOH, it further suffered a contraction of 30 cc. Determine the molecular formula of the hydrocarbon. *Ranchi U*. 1979. Ans. CH_4.

CHAPTER 9

Problems on Thermochemistry :

Thermochemistry is the branch of Physical Chemistry where study of heat effects accompanying chemical and associated physical changes is carried out. Processes, accompanied by the evolution of heat by the system are called exothermic and those, accompained by the absorptian of heat, called endothermic.

Heat of reaction or heat change :

Amount of heat either evolved or absorbed during a chemical reaction is termed as heat of reaction or heat change. The difference in the sum of the heat contents of the reactants from the sum of the heat contents of the reaction products at constant pressure and definite temperature while every substance in a definite physical state is defined as the *heat of reaction.*

Heat of reaction = sum of heat content of the products—sum of heat content of the reactants. $\Delta H = \Sigma H_P - \Sigma H_R$. Heat of evolution is denoted by—ΔH whereas heat absorption by $+\Delta H$.

Heat of reaction at constant volume and that at constant pressure. In certain reactions, specially homogeneous gaseous reactions, volume is kept constant. Heat change accompanying such reacttions is called heat of reaction at constant volume, Q_v or ΔU_v, where ΔU_v is the change in internal energy at constant volume. While, heat change in reactions studied at constant pressure is denoted by Q_p or ΔH_p, where, ΔH_p is the change in heat content or enthalpy change at constant pressure. Q_p and Q_v are connected by the relation $Q_p = Q_v + (\Delta n)\,RT$. Where Δn is the change in number of moles due to the reaction.

Heat of formation : It is the amount of heat either evolved or absorbed per gm molecule of the substance formed out of its constituent elements in the specified state.

Example : $C + O_2 = CO_2 + 94{,}000$ cals. Heat of formation of CO_2 is $+94{,}000$ cals. or, $\Delta H = -94{,}000$ cals.

Heat of combustion: It is the quantity of heat evolved during the process of combustion of one gm molecule of the compound in plenteous oxygen. Example: $CH_4+2O_2=CO_2+2H_2O+212{\cdot}8K$ cals.
Heat of combustion of methane is $+212{\cdot}8K$ cals or $\Delta H=-212{\cdot}8$ K cals.

Heat of solution: It is defined as the quantity of heat either evolved or absorbed when one gm molecule of a solute is dissolved in plenteous quantity of a solvent so that on further dilution no more thermal effects are noted. When this stage of dilution is reached, symbol 'aq' or 'Aq' is used. Example: $HCl+aq=HClaq+17{,}530$ cals. $\Delta H=-17{,}530$ cals.

Heat of neutralisation: It is the amount of heat evolved during the neutralisation of a gm equivalent of an acid by a base. Heat of neutralisation of a strong acid and a strong base is found to be constant according to Hess, equal to 13·7K cals.

Example: $HCl+NaOH=NaCl+H_2O+13680$ cals. Where, "13680 cals" is the amount of heat evolved during neutralisation reaction.

or, $H^++Cl^-+Na^++OH^-\rightarrow Na^++Cl^-+H_2O+13680$ cals.

or, $H^++OH^-\rightarrow H_2O+13680$ cals. Hence, the heat of neutralisation is actually the heat of formation of a gm molecule of water from a gm ion of hydrogen and a gm ion of hydroxyl radical. But when a weak acid or a weak base gets neutralised, the heat of neutralisation changes remarkably from the value 13·7K cals because of incomplete dissociation of weak electrolytes into ions. The concept of *heat of ionization* in place of *heat of neutralisation* must be introduced in that case.

Heat of transition: The heat change occurred when a substance changes from one modification into another *viz.*

heat change for α-sulphur into β-sulphur is known as *heat of transition*.

Standard state of an element: The state at which an element exists at 25°C and 1 atm is called standard state of that element.

Laws of Thermochemistry : *1st law* i.e., Laplace and Lavoisier law. The law states that heat of formation of a compound is equal to the heat of decomposition of the compound into its constituent elements with sign reversed.

Example : If $A+B \rightarrow AB+X$ cals then $AB \rightarrow A+B-X$ cals.

2nd law : Hess's law of constant heat summation : The law states that whenever a chemical process is carried out in a step or, alternatively, in a variety of intermediate steps, total amount of heat evolved in the single step equals to sum of the heat evolved in the intermediate steps provided initial and final stages are the same in both cases.

Example : (i) $C+\frac{1}{2}O_2=CO+X$ cals.

(ii) $CO+\frac{1}{2}O_2=CO_2+Y$ cals.

Alternatively, $C+O_2=CO_2+Z$ cals.

According to the law, $Z=X+Y$.

N. B. Intrinsic or internal energy of any element is arbitarily taken as zero at constant temperature to solve numerical problems. Heat contents of all elements in their standard states are also arbitarily taken to be zero. By convention, heat content of $H^+=0$; heat content of OH^- = heat content of H_2O − heat of neutralisation.

Solved problems :

1. Heat of combustion of diamond at 25°C is 94,480 cals (evolution) and that of graphite at the same temperature is 94,000 cals (evolution). Calculate the heat of conversion of diamond into graphite at 25°C. *Calcutta* U. *1959*.

$C_{(diamond)}+O_2(g) \rightarrow CO_2(g)+94,480$ cals.

$C_{(graphite)}+O_2(g) \rightarrow CO_2(g)+94,000$ cals.

By subtraction ; $C_{(diamond)}-C_{(graphite)} \rightarrow 480$ cals.

or, $C_{(diamond)} \rightarrow C_{(graphite)}+480$ cals.

$\therefore$ $\Delta H298=-480$ cals.

2. Calculate the heat of formation of sulphur trioxide from the following data :

(a) $PbO+S+\frac{3}{2}O_2=PbSO_4+165{\cdot}6K$ cals.
(b) $PbO+H_2SO_4, 5H_2O=PbSO_4+6H_2O+23{\cdot}3K$ cals.
(c) $SO_3+6H_2O=H_2SO_4, 5H_2O+41{\cdot}1K$ cals.

Calcutta U. *1962* ; *Patna* U. *1967A* ; *Magadh* U. *1977.*

Subtracting equation number (b) and (c) respectively from equation (a) we can write

$PbO+S+\frac{3}{2}O_2=PbSO_4+165{\cdot}6K$ cals
$-PbO-H_2SO_4, 5H_2O=-PbSO_4-6H_2O-23{\cdot}3K$ cals
$-SO_3-6H_2O \quad =-H_2SO_4, 5H_2O-41{\cdot}1K$ cals

$\therefore \quad S+\frac{3}{2}O_2-SO_3=165{\cdot}6K$ cals $-\,64{\cdot}4K$ cals
or, $S+\frac{3}{2}O_2=SO_3+101{\cdot}2K$ cals.

3. If the heat of neutralisation of CuO by HCl is 15,270 cals per mole of oxide and the heat of dilute solution of anhydrous $CuCl_2$ is 11,080 cals. Calculate the heat of formation of anhydrous $CuCl_2$ from its elements ; given that the heat of formation of CuO is 37,160 cals, that of water is 68,360 cals and that of dilute HCl from H_2, Cl_2 and water is 39,315 cals per mole.

Calcutta U. 1964.

From the question

$CuO+2HClaq=CuCl_2aq+H_2O+15{,}270$ cals... (i)
$CuCl_2+aq=CuCl_2aq+11{,}080$ cals ... (ii)
$Cu+\frac{1}{2}O_2=CuO+37{,}160$ cals ... (iii)
$H_2+\frac{1}{2}O_2=H_2O+68{,}360$ cals ... (iv)
$\frac{1}{2}H_2+\frac{1}{2}Cl_2+aq=HClaq+39{,}315$ cals ... (v)

(i) +(iii)+2×(v)−(ii)−(iv) gives

$CuO+2HCl\,aq=CuCl_2.aq+H_2O+15{,}270$ cals.
$Cu+\frac{1}{2}O_2=CuO+37{,}160$ cals
$H_2+Cl_2+aq=2HClaq+78630$ cals
$-CuCl_2-aq=-CuCl_2aq-11{,}080$ cals
$-H_2-\frac{1}{2}O_2=-H_2O-68{,}360$ cals

$\therefore \quad Cu+Cl_2-CuCl_2=131{,}060$ cals $-\,79{,}440$ cals or, $Cu+Cl_2=CuCl_2+51{,}620$ cals

The heat of formation of anhydrous cuprous chloride

$=-51{,}620$ cals.

4. Calculate the heat of formation of cane sugar from the following data :

(a) $C+O_2=CO_2$; $\Delta H=-94{,}000$ cals.

(b) $2H_2+O_2=2H_2O$; $\Delta H=-136{,}000$ cals

(c) $C_{12}H_{22}O_{11}+12O_2=12CO_2+11H_2O$; $\Delta H=-1{,}350{,}000$ cals.

Calcutta U. *1969.*

We have according to the question,

(a) $C+O_2=CO_2+94{,}000$ cals.

(b) $2H_2+O_2=2H_2O+136{,}000$ cals.

(c) $C_{12}H_{22}O_{11}+12O_2=12CO_2+11H_2O+1{,}350{,}000$ cals.

$12\times(a)+\frac{11}{2}\times(b)-(c)$ gives,

$12C+12O_2=12CO_2+1{,}128{,}000$ cals.

$11H_2+\frac{11}{2}O_2=11H_2O+748{,}000$ cals.

$-C_{12}H_{22}O_{11}-12O_2=-12CO_2-11H_2O-1{,}350{,}000$ cals.

$\therefore\ 12C+11H_2+\frac{11}{2}O_2-C_{12}H_{22}O_{11}=1{,}876000$ cals $-$ $1{,}350{,}000$ cals.

or, $12C+11H_2+\frac{11}{2}O_2=C_{12}H_{22}O_{11}+526{,}000$ cals.

Hence, the heat of formation of cane sugar is 526,000 cals i.e. ; $\Delta H=-526{,}000$ cals.

5. Given the following heats of reaction at 25°C :

$C_2H_4(g)+3O_2(g)=2CO_2(g)+2H_2O(l)$, $\Delta H=-3337{\cdot}3K$ cals.

$2H_2(g)+O_2(g)=2H_2O(l)$, $\Delta H=-136{\cdot}6K$ cals.

$2C_2H_6(g)+7O_2(g)=4CO_2(g)+6H_2O(l)$, $\Delta H=-745{\cdot}6K$ cals.

Calculate ΔH for the reaction

$C_2H_4(g)+H_2(g)=C_2H_6(g)$ at 25°C.

Bombay U. 1967 ; Calcutta U. 1971.

Arranging 2nd equation as

$$H_2(g)+\tfrac{1}{2}O_2(g)=H_2O(l),\qquad \Delta H=-\frac{136{\cdot}6K\text{ cal.}}{2}=-68{\cdot}3K\text{ cal.}$$

Adding up this equation with 1st equation

$C_2H_4(g)+H_2(g)+\frac{7}{2}O_2(g)=2CO_2(g)+3H_2O(l)$

$\triangle H=-3337{\cdot}3-68{\cdot}3=-3405{\cdot}6$K cals. From this equation and third equation,

we can write,

$C_2H_4(g)+H_2(g)+2CO_2(g)+3H_2O(l)+\frac{7}{2}O_2(g)$
$=C_2H_6(g)+\frac{7}{2}O_2(g)+2CO_2(g)+3H_2O(l)$

$\Delta H=(372{\cdot}8-3405{\cdot}6)$K cals $=-3032{\cdot}8$K cals.

or, $C_2H_4(g)+H_2(g)=C_2H_6(g)$

6. Find out the heat of formation of anhydrous aluminium chloride from the following reactions.

(1) $2Al+6HCl\ aq=Al_2Cl_6aq+3H_2+239760$ cals.
(2) $H_2+Cl_2=2HCl+44000$ cals.
(3) $HCl+aq=HClaq+17315$ cals.
(4) $Al_2Cl_6+aq=Al_2Cl_6aq+153690$ cals.

Ranchi U. 1968A ; Rajasthan U. 1968 ; Vikram U. 1973.

From equation (2) $H(6HCl)=-3\times44000$ cals.

From equation (3) $H(6HClaq)=-3\times44000$ cals -6×17315 cals $+6$ aq.

From equation (1) $H(Al_2Cl_6aq)=-3\times44000$ cals -6×17315 cals $+6$ aq -239760 cals.

From equation (4) $H(Al_2Cl_6)=153690-3\times44000-6\times17315-239760+6aq.-aq.=-321960$ cals.

$\therefore\ H_F(Al_2Cl_6)=321960$ cals.

Where H & H_F represent heat content & heat of formation respectively. It is to be pointed out that 'aq' term cancels each other it does not matter if one of them contains 6 molecules.

7. The heats of combustion of rhombic sulphur and monoclinic sulphur are 70960 and 71030 calories. Calculate the heat of transition of rhombic to monoclinic sulphur. *Rajasthan U. 1971.*

$S_{(rhombic)}+O_2\rightarrow SO_2+70960$ cals. ... (i)

$S_{(monoclinic)}+O_2\rightarrow SO_2+71030$ cals ... (ii)

(i) − (ii) *gives*

$S_{(\text{rhombic})} \rightarrow S_{(\text{monoclinic})} + (70960 - 71030)$ cals.

or, $S_{(\text{rhombic})} \rightarrow S_{(\text{monoclinic})} - 70$ cals.

The heat of transition of rhombic to monoclinic sulphur = 70 cals. (∵ transition reaction is endothermic)

8. Calculate the heat of formation of benzene having given that heats of combustion of benzene, carbon and hydrogen are 754,300 cals, 94,380 cals and 68,380 cals respectively.

Rajasthan U. 1970; *Ravi Shankar* U. *1973.*

(a) $C_6H_6 + \frac{15}{2}O_2 = 6CO_2 + 3H_2O + 754{,}300$ cals.

(b) $C + O_2 = CO_2 + 94{,}380$ cals.

(c) $H_2 + \frac{1}{2}O_2 = H_2O + 68{,}380$ cals

$6 \times (b) + 3 \times (c) - (a)$ gives,

$$6C + 6O_2 = 6CO_2 + 566{,}280 \text{ cals.}$$
$$3H_2 + \tfrac{3}{2}O_2 = 3H_2O + 205{,}140 \text{ cals.}$$
$$-C_6H_6 - \tfrac{15}{2}O_2 = -6CO_2 - 3H_2O - 754{,}300 \text{ cals}$$

∴ $6C + 3H_2 - C_6H_6 = 771{,}420 \text{ cals} - 754{,}300$ cals.

or, $6C + 3H_2 = C_6H_6 + 17{,}120$ cals.

Hence, the heat of formation of benzene is 17,120 cals i.e., $\Delta H = -17{,}120$ cals.

9. When one mole of liquid benzene is burnt completely in oxygen to form liquid water and carbondioxide, ΔH is $-783{\cdot}4$K cal at 18°C. Calculate the heat of this reaction at constant volume at the same temperature.

Rajasthan U. *1969*; *Panjab* U. *1971.*

$C_6H_6(l) + \frac{15}{2}O_2(g) = 6CO_2(g) + 3H_2O(l) + 783{\cdot}4\text{K cal.}$

Here, $\Delta n = n_2 - n_1 = 6 - \frac{15}{2} = -\frac{3}{2}$.

Now, $Q_p = Q_v + (\Delta n)RT$.

$-783{\cdot}4 = Q_v - \frac{3}{2} \times 2 \times (273 + 18) = Q_v - 873$

∴ $Q_v = 873 - 783{\cdot}4 = 89{\cdot}6\text{K}$ cals.

10. One mole of Naphthalene was burnt in oxygen gas at constant volume to give carbondioxide gas and water at 25°C.

The heat evolved in the reaction was found to be 1228·2K cal. Calculate the heat of combustion of Naphthalene at constant pressure.

[R = 0·002*K* cal./mole. degree] *Rajasthan* U. *1976*.

We have, $Qp = Qv + (\Delta n)RT$

$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l) + 1228{\cdot}2K$ cals.

$\therefore \quad Qp = -1228{\cdot}2 - 2 \times 0{\cdot}002 \times 298$

$\because \quad \Delta n = n_2 - n_1 = 10 - 12 = -2$

or, $\Delta Hp = -1229{\cdot}392K$ cals.

11. Heats of combustion of hydrogen, carbon and methane at constant pressure at 27°C, are 68·3K cal, 94·0K cal. and 212·6K cal respectively Calculate the heat of formation of methane at constant volume at 27°C. *Patna* U. *1968* ; *Panjab* U. *1974* ; *Burdwan* U. *1975* ; *Calcutta* U. *1977*.

(a) $H_2 + \frac{1}{2}O_2 = H_2O + 68{\cdot}3K$ cals.

(b) $C + O_2 = CO_2 + 94{\cdot}0K$ cals.

(c) $CH_4 + 2O_2 = CO_2 + 2H_2O + 212{\cdot}6K$ cals.

$2 \times (a) + (b) - (c)$ give,

$2H_2 + O_2 = 2H_2O + 136{\cdot}6K$ cals.

$C + O_2 = CO_2 + 94{\cdot}0K$ cals.

$-CH_4 - 2O_2 = -CO_2 - 2H_2O - 212{\cdot}6K$ cals.

$\therefore \quad C + 2H_2 = CH_4 + (136{\cdot}6 + 94{\cdot}0 - 212{\cdot}6)K$ cals.

or, $C + 2H_2 = CH_4 + 18K$ cals.

$Qp = Qv + (\Delta n)RT$

or, $Qv = Qp - (\Delta n)RT$. Here, $\Delta n = 1 - 2 = -1$.

$Qv = -18 - 1 \times 0{\cdot}002 \times 300 = -18 - 0{\cdot}6 = -18{\cdot}6K$ cals.

12. From the following thermochemical equations, all of which refer to a temperature of 17°C at constant pressure, calculate the heat evolved in the polymerisation of acetylene to benzene (a) at constant volume, and (b) at constant pressure.

$C + O_2 = CO_2 + 96{,}960$ cals ... (i)

$2H_2 + O_2 = 2H_2O(l) + 136{,}720$ cals ... (ii)

$2C_6H_6+15O_2=12CO_2+6H_2O(l)+1{,}598{,}700$ cals (iii)

$2C_2H_2+5O_2=4CO_2+2H_2O(l)+620{,}100$ cals (iv)

Behrampur U. *1970*

$3\times$(iv)$-$(iii) gives,

$$6C_2H_2+15O_2=12CO_2+6H_2O(l)+1860{,}300 \text{ cals.}$$
$$\underline{2C_6H_6+15O_2=12CO_2+6H_2O(l)+1{,}598{,}700 \text{ cals.}}$$
$$6C_2H_2-2C_6H_6=261{,}600 \text{ cals.}$$

or, $3C_2H_2=C_6H_6+130{,}800$ cals.

Hence, the heat of polymerisation of acetylene to benzene at constant pressure is 130,800 cals.

Now, $Qp=Qv+(\Delta n)RT$ or, $Qv=Qp-\Delta nRT$.

Here, $\Delta n=-2$. $\therefore$ $Qv=-130{,}800+2\times2\times290$

or, $Qv=-130{,}800+1160=-129{,}640$ cals.

13. Find out the heat of formation of CO at 17°C from the following reactions. *M.* U. *1976A* ; *Jiwaji 1970S* ; *Poona 1960.*

(i) $C+O_2=CO_2+97000$ cals

(ii) $CO+\frac{1}{2}O_2=CO_2+68000$ cals.

Let the heat of formation of CO be 'X' cals.

Then, $C+\frac{1}{2}O_2=CO+X$ cals

$$\underline{CO+\tfrac{1}{2}O_2=CO_2+68000 \text{ cals}}$$
$$C+O_2=CO_2+X \text{ cals}+68000 \text{ cals.}$$

Again, $C+O_2=CO_2+97000$ cals.

Hence, $X+68000=97000$

$\therefore$ $X=29000$ cals.

14. Calculate the heat of formation of Na_2O from the following data :—

(1) $Na+H_2O(l)=NaOH+\frac{1}{2}H_2+43200$ cals.

(2) $Na_2O+H_2O(l)=2NaOH+63200$ cals.

(3) $H_2+\frac{1}{2}O_2=H_2O(l)+68000$ cals.

$2\times1)+3)-2)$ give,

$$\begin{array}{lcl} 2Na+2H_2O(l)=2NaOH=\frac{2}{2}H_2+2\times 43200 \text{ cals.} \\ H_2+\frac{1}{2}O_2 = H_2O(l) + 68000 \text{ cals.} \\ \underline{-Na_2O-H_2O(l)=-2NaOH - 63200 \text{ cals.}} \\ \therefore\ 2Na+\frac{1}{2}O_2 = Na_2O+(86400+68000-63200) \text{ cals.} \end{array}$$

Or, $2Na+\frac{1}{2}O_2=Na_2O+91200$ cals.

The heat of formation of $Na_2O=-91200$ cals.

15. The heat of neutralisation of a weak acid in normal solution by a strong alkali is 13,385 cals. Assuming that the acid is 14% dissociated in normal solution, calculate the heat of dissociation of the acid. If the acid were cent percent dissociated, the amount of heat evolved would be 13680 cals.

Therefore the amount of heat (evolved) in the dissociation of 86% of the acid $=13680-13385=295$ cals.

$\therefore$ the amount of heat of dissociation per gm.

$$\text{equivalent}=-\frac{295\times 100}{86}=-343{\cdot}0232 \text{ cals.}$$

16. The heats of neutralisation of two acids H*A* and HB are 13,650 cals and 11,200 cals respectively. When 1 gm. equivalent of sodium hydroxide in dilute solution is added to a mixture of 1 gm. equivalent of HA and 1 gm. equivalent of HB, 12,960 cals are evolved. Compare the strengths of the two acids, HA and HB.

Let a fraction n gm. equivalent of the sodiumhydroxide get neutralised by the acid HA.

Then $n\ HA+n\ NaOH\rightarrow n\ NaA+nH_2O+(n\times 13650)$ cals. Since there is only 1 gm. equivalent of NaOH, $(1-n)$ gm. equivalent must get neutralised by the acid, HB. Therefore

$$(1-n)HB+(1-n)NaOH=(1-n)NaB+(1-n)H_2O$$
$$+[(1-n)\times 11200] \text{ cals.}$$

But the apparent heat of the reaction is, 12,960 cals.

$$\therefore\ (n\times 13650)+[(1-n)\times(11200)]=12960$$

$$\therefore\ n=0{\cdot}72 \text{ and } (1-n)=0{\cdot}28.$$

$$\text{So, } \frac{\text{the strength of acid, HA}}{\text{the strength of acid, HB}}=\frac{0{\cdot}72}{0{\cdot}28}=2{\cdot}57:1.$$

17. For the reaction C (graphite)$+\frac{1}{2}O_2=CO$ at 298°K and 1 atm, $\Delta H=-26416$ cals, what is ΔE, if the molar volume of graphite is 0·0053 litres. You may assume ideal gas conditions.

Punjab. U. *1975.*

We have, $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$; Or, $\frac{1\times V_1}{273}=\frac{1\times 0{\cdot}0053}{298}$

Or, $V_1=\frac{0{\cdot}0053\times 273}{298}$

$\therefore$ number of moles of C (graphite) $=\frac{0{\cdot}0053}{298}\times\frac{273}{22{\cdot}4}$

Or, number of moles of C (graphite)$=0{\cdot}0002168$.

Now, $\Delta n=1-0{\cdot}5-0{\cdot}0002168=0{\cdot}4997832\simeq 0{\cdot}5$.

$Qp=Qv+0{\cdot}5\times 2\times 298=Qv+298$

Or, $-26416=Qv+298$ or, $Qv=-26714$ cals.

$\because$ $Qv=\Delta E$ $\therefore$ $\Delta E=-26714$ cals.

18. When one mole of water at 100°C is converted into steam at a pressure of one atmosphere, 9720 calories of heat are absorbed. The molar volumes of water and steam are 18 and 30,600 mls. respectively. Calculate ΔE of the process.

Kurukshetra U. *1975.*

We have, $Qp=Qv+\Delta n\ RT$.
$9720=Qv+\Delta n\ RT$.

Now, $\Delta n\ RT=PV=\frac{1\times(30600-18)\times 2}{1000\times 0\ 0821}$ cals.

or, $\Delta n\ RT=745$ cals. $\therefore$ $Qv=9720-745=8975$ cals.

$\therefore$ $\Delta E=8975$ cals $\because$ $Qv=\Delta E=\Delta Uv=$the change in internal energy at constant volume. [0·0821 lit. atm. =2 cals.]

Bond energies and dissociation energies

The energy required to break a given bond in some specific compound is defined as the **bond dissociation energy**. It is a definite quantity. It depends on the presence of other groups in a molecule.

Example : The energy required to break O–H bond in water is 498KJ. Thus H—O—H (g)→H(g)+OH (g — 498 KJ mol^{-1}.

$\therefore$ $\Delta H_{298} = 498$ KJ mol^{-1}. Again, the energy required to break the O—H bond in hydroxyl group is 430 KJ mol^{-1}.

Thus $O{-}H\,(g) \rightarrow O\,(g) + H\,(g) - 430$ KJ mol^{-1}

$\therefore$ $\Delta H_{298} = 430$ KJ mol^{-1}

[Temperature is 25°C i.e., 298°K, considered]

Hence, the bond dissociation energy of O—H linkage in water molecule is 498 KJ mole^{-1} where as that in a hydroxyl group is only 430 KJ mol^{-1}. The average of dissociation energies of a given bond in a series of different dissociating species, is known as **bond energy.** In case of diatomic molecules the bond energy and bond dissociation energies are identical where as it is different in case of polyatomic molecules. The O—H bond energy in water molecule is the average of the two bond dissociation energies.

$$\therefore \quad \Delta H_{O-H} = \frac{498+430}{2} = 464 \text{ KJ mol}^{-1}.$$

Solved problems :

1. C—H bond energy in methane

As all the four C—H bonds in methane are equivalent, the average of the four bond dissociation energies would be equal to the C—H bond energy.

$$C\,(g) + 4H(g) \rightarrow CH_4(g) \quad \Delta H_{298} = ?$$

Data given : (i) $C\text{ (graphite)} \xrightarrow{\text{Sublimation}} C(g) \Delta H_{298} = 716{\cdot}68\text{KJ}$

(ii) $\frac{1}{2}H_2(g) \xrightarrow{\text{Dissociation}} H(g) \;\Delta H_{298} = 217{\cdot}97$ KJ

(iii) $C\text{ (graphite)} + 2H_2(g) \xrightarrow{\text{fusion}} CH_4\,(g) \Delta H_{298} = -74{\cdot}75$ KJ

Multiply equation (ii) by 4 then reverse this new equation and also reverse equation (i). Now combine these two new equations with equation (iii) to get.

$$C\,(g) + 4H\,(g) \rightarrow CH_4\,(g)$$
$$\Delta H_{298} = -1663{\cdot}31 \text{ KJ}.$$

Thus, the average bond energy for C—H linkage is

$$\Delta H_{C-H}=\frac{1663{\cdot}34}{4}=415{\cdot}8KJ.$$

2. Find the enthalpy of formation of H_2O i.e., ΔH_f. In this reaction the H—H bond (bond energy 433KJ mol^{-1}) and 0=0 bond (bond energy 492 KJ mol^{-1}) are broken and two O—H bonds (bond energy 464 KJ $mole^{-1}$) are formed.

Consider the reaction, $H_2\ (g)+\frac{1}{2}\ O_2\ (g)\rightarrow H_2O\ (g)\quad \Delta H_f=\ ?$

Given : (i) $H_2\ (g)\rightarrow 2H\ (g)—433\ KJ\ mole^{-1}$

$\Delta H=+433\ KJ\ mol^{-1}$

(ii) $\frac{1}{2}\ O_2(g)\ \rightarrow\ O\ (g)—\frac{492}{2}\ KJ\ mol^{-1}$

$\Delta H=+246\ KJ\ mol^{-1}$

(iii) $2\ O—H\ (g)\rightarrow 2\ O\ (g)\ +\ 2H\ (g)—2\times 464KJ$

$\Delta H=+928\ KJ\ mol^{-1}$

or, $2\ O—H\ (g)—O\ (g)\rightarrow 2O\ (g)—O\ (g)+2H\ (g)—928KJ$

or, $H_2O\ (g)\rightarrow O\ (g)\ +\ 2H\ (g)-928\ KJ$

or, $O\ (g)+2H\ (g)\rightarrow H_2O\ (g)+928\ KJ\quad \Delta H=-928\ KJ\ mol^{-1}$

Adding (i), (ii) and modified (iii) we get,

$H_2\ (g)+\frac{1}{2}\ O_2\ (g)\rightarrow H_2O(g)\quad \Delta H_f=(433+246—928)$
$KJ\ mol^{-1}=—249\ KJ\ mol^{-1}$.

3. Calculate the bond energy of HCl given that the H—H bond energy is 433 KJ mol^{-1}, Cl—Cl bond energy is 242 KJ mol^{-1} and ΔH_f for HCl is —91 KJ $mole^{-1}$.

(i) $H_2\ (g)\rightarrow 2H\ (g)—433\ KJ\quad \Delta H=433\ KJ\ mol^{-1}$.

(ii) $Cl_2\ (g)\rightarrow 2Cl\ (g)—242\ KJ\quad \Delta H=242\ KJ\ mol^{-1}$

(iii) $H\ (g)\ +\ Cl\ (g)\rightarrow HCl\ (g)\ +QKJ\quad \Delta H=—QKJ\ mol^{-1}$

or, $2H\ (g)+2Cl\ (g)\rightarrow 2HCl\ (g)\ +\ 2QKJ\qquad \Delta H=—2QKJ$

Adding (i), (ii) and modified (iii) we get,

$H_2\ (g)\ +\ Cl_2\ (g)\ \rightarrow\ 2HCl\ (g)\quad \Delta H=(433+242-2Q)KJ$

By the question, $433+242—2Q=-91\times 2$

$$\therefore\ Q=\frac{433+242+182}{2}=\frac{857}{2}=428{\cdot}5\ KJ\ mol^{-1}$$

$\equiv 50 \times 0{\cdot}5$ cc (N)NaOH $= 25$ cc (N)NaOH = volume of alkali taken.

25 cc diluted final solution $\equiv 14$ cc $0{\cdot}1$(N) H_2SO_4

$\equiv 14 \times 0{\cdot}1$ cc (N) H_2SO_4

$\therefore$ 250 cc diluted final soln $\equiv \frac{14 \times 0{\cdot}1 \times 250}{25}$ cc (N)

$H_2SO_4 = 14$ cc (N) $H_2SO_4 \equiv 14$ cc (N) NaOH

= Volume of alkali unused. $\therefore$ Vol of alkali used $= (25 - 14)$ cc (N)NaOH $= 11$ cc (N)NaOH. Now, from the equation,

2000 cc (N) NaOH $\equiv 249$ gm copper sulphate crystal (pure)

$\therefore$ 11 cc (N) NaOH $\equiv \frac{249 \times 11}{2000} = 1{\cdot}3695$ gm " ".

$1{\cdot}5$ gm impure copper sulphate crystals contain $1{\cdot}3695$ gm pure coppersulphate

$\therefore$ 100 " " " " $\frac{1{\cdot}3695 \times 100}{1{\cdot}5} = 91{\cdot}3$ ".

The percentage of pure $CuSO_4,5H_2O$ in the impure sample $= 91{\cdot}3$.

19. A solution containing 10 cc of H_2SO_4 and HCl required 16 cc of N/8 NaOH soln. for complete neutralisation. 20 cc of the above acid soln. when treated with excess of $BaCl_2$ soln gave $0{\cdot}3501$ gm $BaSO_4$. Find the weight of HCl present per litre of the above acid soln. *West Bengal Joint Entrance Examination 1976.*

10 cc of H_2SO_4 and HCl $\equiv 16$ cc N/8 NaOH

$\equiv \frac{16}{8}$ cc (N) NaOH $= 2$ cc (N) NaOH.

$\therefore$ 20 cc of H_2SO_4 and HCl $\equiv 4$ cc (N) NaOH.

Let the volume of (N) NaOH consumed by $H_2SO_4 = X$ cc ;

$\therefore$ volume of (N) NaOH consumed by HCl $= (4 - X)$ cc.

We know, $H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl$

2000 cc (N) 233 gms ; 233 gm $BaSO_4$, precipitatedout from 2000 cc (N) H_2SO_4 $\therefore$ $0{\cdot}3501$ gm $BaSO_4$, precipitatedout from $\frac{2000 \times 0{\cdot}3501}{233} = 3$ cc (N) H_2SO_4. So, 3 cc (N) $H_2SO_4 \equiv 3$ cc (N) NaOH $= X$ cc (N) NaOH.

∴ Volume of (N)NaOH consumed by HCl = (4 − 3) cc = 1 cc.

Now, 1 cc (N) NaOH ≡ 1 cc (N) HCl.

Again, 1000 cc (N) HCl contain 36·5 gm. HCl.

∴ 1 cc (N) HCl contains $\frac{36{\cdot}5}{1000} = 0{\cdot}0365$ gm HCl.

20 cc acid mixture contain 0·0365 gm HCl.

1000 cc (1 litre) " " $\frac{0{\cdot}0365 \times 1000}{20} = 1{\cdot}825$ gm HCl.

20. At 27°C, 4·125 gm of a saturated solution of a metal carbonate require 69 ml of a 0·25(N) H_2SO_4 soln for neutralisation. Find the solubility of the metal carbonate if its eq wt is 53. *Bombay F. Y. Sc. 1975.*

69 ml 0·25 (N) $H_2SO_4 \equiv$ 69 ml 0·25 (N) metal carbonate

≡ 69 × 0·29 ml (N) metal carbonate = 20·01 ml (N) metal carbonate.

Now, 1000 ml (N) metal carbonate contain 53 gm metal carbonate

∴ 20·01 " " " " " $\frac{53 \times 20{\cdot}01}{1000} = 1{\cdot}06$ ".

As, wt of metal carbonate saturated soln = 4·125 gms ;

wt of metal carbonate = 1·06 gm.

∴ wt of water = 4·125 − 1·060 = 3·065 gm.

3·065 gm water contain 1·06 gm metal carbonate

100 gm " " $\frac{1{\cdot}06 \times 100}{3{\cdot}065} = 34{\cdot}584$

∴ solubility = 34·584.

21. Upon heating a litre of a N/2 HCl soln, 2·675 gms of hydrogen chloride are lost and the volume of the solution shrinks to 750 ml. Calculate (i) the normality of the resultant soln and (ii) the number of milliequivalents of HCl in 100 ml of the original soln. *I.I.T. (Group A). 1975.*

(i) 1000 cc (N) HCl contain 36·5 gm HCl

∴ 1000 cc $\left(\frac{N}{2}\right)$ HCl contain $\frac{36{\cdot}5}{2} = 18{\cdot}25$ gm HCl. Initial amount of HCl = 18·25 gms ; amount of HCl lost = 2·675 gms.

$\therefore$ amount of HCl remains unreacted

$=(18{\cdot}25-2{\cdot}675)$ gms $=15{\cdot}575$ gms.

Volume of the resultant solution = 750 ml.

750 ml solution contain 15·575 gm HCl

1000 ml " " $\frac{15{\cdot}575\times1000}{750}=20{\cdot}766$ gm HCl $=\frac{20{\cdot}766}{36{\cdot}5}$

gm. eq HCl = 0·5689gm eq HCl.

Strength of the resultant soln = 0·57(N).

(ii) 1000 ml original hydrochloric acid soln contain $\frac{1}{2}$ gm eq HCl.

i.e., " " " " $\frac{1}{2}\times1000=500$ milli eq HCl.

$\therefore$ 100 " " " $\frac{500\times100}{1000}=50$ milli eq HCl.

22. An alkaline soln contains both NaOH and Na_2CO_3. 25 cc of this soln require for neutralisation 15 cc of 0·1 (N) HCl, when phenolphthalein is used as an indicator. But on adding methyl orange, the soln is found to be alkaline even now and requires 9 cc more of the same acid for complete neutralisation. Calculate the weights of NaOH and Na_2CO_3 in one litre of the alkaline soln. *Bihar.* U. *1967A*, *'70A.*

In the first case of titration, phenolphthalein indicator detects the end point when all the NaOH and half of Na_2CO_3 are neutralised and at this point Na_2CO_3 is converted into $NaHCO_3$ which is not alkaline to phenolphthalein.

Reactions : (i) $NaOH+HCl=NaCl+H_2O$;

(ii) $Na_2CO_3+HCl=NaHCO_3+NaCl$.

In the 2nd case of titration, methyl orange alters colour when all the NaOH and Na_2CO_3 are neutralised.

Reactions : (i) $NaOH+HCl=NaCl+H_2O$;

(ii) $Na_2CO_3+2HCl=2NaCl+H_2O+CO_2$. (In the 2nd case, this reaction, $NaHCO_3+HCl=NaCl+H_2O+CO_2$ also takes place)

Volume of acid added in 1st titration = 15 cc 0·1 (N) HCl = all the NaOH + half the Na_2CO_3 of the mixture.

Volume of acid added in 2nd titration $=(15+9)$ cc 0·1(N)HCl
$=$all the NaOH$+$all the Na_2CO_3 of the mixture.
$\therefore$ 9 cc 0·1 (N) HCl$=$half the Na_2CO_3 in the mixture.
$\therefore$ the amount of NaOH in 25 cc of the mixture
$=(15-9)=6$ cc 0·1(N)
HCl$\equiv$6 cc 0·1 (N)NaOH$\equiv\frac{6}{10}$ cc (N) NaOH$=$0·6 cc (N)NaOH.
1000 cc (N) NaOH soln contain 40 gm NaOH
$\therefore$ 0·6 cc (N) NaOH soln contain $\frac{40\times 0{\cdot}6}{1000}=0{\cdot}024$ gm
NaOH i.e., 25 cc mixed alkali soln contain 0·024 gm NaOH.
$\therefore$ 1000 cc mixed alkali soln contain $\frac{0{\cdot}024\times 1000}{25}$
$=$0·96 gm NaOH.
The amount of Na_2CO_3 in 25 cc of the mixture
$=2\times 9$ cc 0·1 (N) HCl
$=$18 cc 0·1 (N) HCl$\equiv$18 cc 0·1 (N) Na_2CO_3 soln
$\equiv 18\times 0{\cdot}1$ cc (N) Na_2CO_3 soln.
$=$1·8 cc of (N) Na_2CO_3 soln.
1000 cc (N) Na_2CO_3 soln contain 53 gm Na_2CO_3.
$\therefore$ 1·8 cc (N) Na_2CO_3 soln contain $\frac{53\times 1{\cdot}8}{1000}$
$=$0·0954 gm Na_2CO_3.
i.e., 25 cc mixed alkali soln contain 0·0954 gm Na_2CO_3
$\therefore$ 1000 cc " " " " $\frac{0{\cdot}0954\times 1000}{25}$
$=$3·816 gm Na_2CO_3.

23. 0·3 gm of a mixture of ammonium chloride and sodium chloride was boiled with an excess of caustic soda solution and the liberated gas was absorbed in 100 cc of 0·112(N) sulphuric acid soln. The excess of the acid was neutralised by 40 cc of a solution of sodium carbonate containing 0·8215 gm of sodium carbonate per 100 cc of the soln. Find out the percentage of ammonium chloride in the mixture. *Calcutta.* U. 1970.

From the last line of the question,
100 cc Na_2CO_3 soln contain 0·8215 gm Na_2CO_3.

$\therefore$ 1000 cc Na_2CO_3 soln contain $\frac{0·8215\times1000}{100}$

$=8·215$ gm $Na_2CO_3=\frac{8·215}{53}$ gm eq.

$Na_2CO_3=0·155$ gm eq Na_2CO_3.

Strength of sodium carbonate soln $=0·155$ (N).

40 cc 0·155 (N) $Na_2CO_3\equiv40$ cc 0·155 (N) H_2SO_4

$\equiv40\times0·155$ cc (N) H_2SO_4

$\equiv\frac{40\times0·155}{0·112}$ cc0·112(N) H_2SO_4.

$=53·36$ cc 0·112 (N) H_2SO_4.

Volume of acid reacted with ammonia

$=(100-53·36)$ cc 0·112 (N) H_2SO_4

$=46·64$ cc 0·112 (N) H_2SO_4.$2NH_3+H_2SO_4=(NH_4)_2SO_4$.

From the equation, 1000 cc (N) H_2SO_4 react with 22·4 litre NH_3.

$\therefore$ 46·64 cc 0·112(N) H_2SO_4 react with $\frac{22·4\times46·64\times0·112}{1000}$

$=0·117$ litre NH_3.

Let the amount of NH_4Cl in the mixture $=$ X gm.

$NH_4Cl+NaOH=NH_3+NaCl+H_2O$; 53·5 gm NH_4Cl reacting with NaOH produce 22·4 litre NH_3. $\therefore$ X gm NH_4Cl reacting with NaOH produces $\frac{22·4X}{53·5}$ litre NH_3.

$\therefore$ $\frac{22·4X}{53·5}=0·117$ or, $X=0·279$ gm ; 0·3 gm mixture contains $\frac{0·279\times100}{0·3}=93$ gm NH_4Cl.

Percentage of ammonium chloride in the mixture is therefore 93.

24. 1 gm of a mixture consisting of equal number of moles of carbonates of two alkali metals, required 44·4 ml of 0·5(N) HCl for complete reaction. If the atomic weight of one of the metals is 7, find the atomic weight of the other metal.

I. I. T. 1972.

X and Y are supposed to be the symbols of two alkalimetals.

Let the atomic weight of Y be a. According to the question atomic weight of X=7. The valency of each alkali metal is taken as unity. The formulae of the carbonates are therefore X_2CO_3 and Y_2CO_3.

1000 ml (N) HCl≡1gm eq carbonate≡$\frac{1}{2}$ gm mole carbonate.

$\therefore$ 44·4 ml 0·5 (N) HCl≡ $\frac{44{\cdot}4\times0{\cdot}5}{2\times1000}=0{\cdot}0111$ gm mole mixed carbonate.

Again, number of gm moles of X_2CO_3 = number of gm moles of $Y_2CO_3=\frac{0{\cdot}0111}{2}$. Weight of X_2CO_3 in 1 gm mixture

$=\frac{0{\cdot}0111}{2}\times74=0{\cdot}4107$ gm.

$\because$ mol wt of $X_2CO_3=2\times7+60=74$. Wt of Y_2CO_3 in 1gm mixture $=1-0{\cdot}4107=0{\cdot}5893$ gm. Mol wt of $Y_2CO_3=2a+60$.

$\therefore\ (2a+60)\frac{0{\cdot}0111}{2}=0{\cdot}5893$ Or, a=23 $\therefore$ atomic weight of Y=23.

N. B. 1gm eq carbonate = eq wt of carbonate

$=\frac{\text{mol wt of carbonate}}{\text{acidity}}=\frac{\text{1 gm mole}}{2}=\frac{1}{2}$ gm mole carbonate.

Here, formula wt = molecular wt (say).

Problems for practice

1. Calculate the molarity and molality of NaCl in a soln which contains 10% by wt of NaCl and has a density of 1·071 gm/ml (mol. wt. of NaCl=58·5). *Calcutta.* U. B. Sc. *1972.* Ans. 1·709 ; 1·595.

2. Calculate the (i) molarity and (ii) molality of Na_2CO_3 in a soln of 25 gm $Na_2CO_3.10H_2O$ in water, the volume of the resulting soln being 200 cc and its density 1·04 gm/cc (mol. wt. of $Na_2CO_3.10H_2O=286$). *Calcutta.* U. B. Sc. *1975.* Ans. 0·437 molar ; 0·4775 molal.

3. Calculate the molality, molarity and solute mole fraction in a 5% (wt/wt) aqueous soln (density = 1·04 gm/cc) of a substance of mol wt 25. *Calcutta.* U. B. Sc. *1977*. Ans. molality = 2·105 ; molarity = 2·08 , mole fraction of solute = 0·03652.

4. What is the molarity and molality of a 13% soln (by wt) of sulphuric acid ? Its density is 1·090 gm/ml. To what volume should 100 ml of this acid be diluted in order to prepare a 1·5(N) solution ? *I. I. T. 1978*. Ans. 1·326 ; 1·216 ; 176·9 cc.

5. Conc H_2SO_4 has a density of 1·84 gm/cc at 25°C and it contains 98% of acid by wt. What volume of the concentrated acid should be used to prepare 1000 litres of 0·5 molar sulphuric acid soln at 25°c ? *I. I. T. 1971*. Ans. 27·17 litres.

6. Calculate the molarity of a concentrated solution of sulphuric acid which is labelled to be 98% sulphuric acid by wt and whose specific gravity is 1·84. *I. I. T. (GPA) 1974*. Ans. 18·4.

7. 25ml of a soln of hydrochloric acid cont aining 7·3 gms of the acid per litre neutralised 30 ml of caustic soda soln. 20 ml of this alkali soln neutralised 24ml of a soln of sulphuric acid. Calculate the normality and strength of sulphuric acid. *Delhi. H. S. 1972*. Ans. 0·139 ; 6·811 gm/litre.

8. Two litres of ammonia at 30°C and at 0·2 atm pressure neutralised 134ml of a soln of sulphuric acid. Calculate the normality of the acid. *I. I. T*. 1978. Ans. 0·1199(N).

9. To 50 ml of a soln of HCl, 25ml of 0·5 N NaOH soln were added. The remaining acid required 20 ml of 0·5 N Na_2CO_3 for complete neutralisation. Calculate the normality of the acid soln. *Bombay. F. Y. Sc.* 1971. Ans. 0·45N.

10. What volume of 6(N) NaOH is needed by 30 ml 4(N) HCl for neutralization ? *L. N. M.* U. 1974A. Ans. 20 ml.

11. 5·3 gms of anhydrous sodium carbonate is dissolved in water and the volume is made up to one litre. 150 ml of this soln require 45 ml of a sulphuric acid soln for complete neutralisation. Calculate the strength of the acid.

Calcutta. U. B. Sc. *1972*. Ans. N/3.

12. 5 gms of Zn were placed in a litre of dil H_2SO_4. After all action has ceased, the excess of Zn remained weighed 1·75 gm. Find the strength of sulphuric acid in terms of normality and also the volume of H_2 liberated at 117°C and 380 mm.

Ranchi. U. *1971.* Ans. N/10 ; 3·2 litres.

13. 22·7 ml of (1·1) N/10 Na_2CO_3 require 10·2 ml of a dilute soln of H_2SO_4 for neutralization. How much of water must be added to 400 ml of this acid soln to make it exactly N/10 ?

L. N. M. U. *1973A.* Ans. 579·2 ml.

14. How many millilitres of concentrated sulphuric acid of specific gravity 1·84 containing 98% H_2SO_4 by wt are required to prepare 200 ml of 0·5 (N) sulphuric acid ? *I. I. T. 1976.*

Ans. 2·7174 ml.

15. A sample of $Na_2CO_3.H_2O$ weighing 0·62 gm is added to 100 ml of 0·1 (N) sulphuric acid soln. Will the resulting soln be acidic, basic or neutral ? *I. I. T.* 1976. Ans. neutral or very feeble acidic due to CO_2.

16. 25cc of an alkali soln is mixed with 8cc of a 0·75 (N) acid soln and for complete neutralisation it further requires 15cc of a 0·8 (N) acid soln. Find the strength of the given alkali soln.

West Bengal J. E. E. 1975. Ans. 0·72(N).

17. What is the volume of 0·05(N) HCl required to neutralise completely 40cc of 0·1(N) sodium hydroxide.

Hyderabad. I.Sc. 1977. Ans. 80cc.

18. 10cc of conc H_2SO_4 (d=1·83) is diluted with water to form one litre of the soln. 10cc of this soln require 17·5cc of 0·2(N) caustic soda soln for neutralisation. What was the percentage of sulphuric acid in the acid ? *West Bengal* H.S. *1975.*

Ans. 93·715.

19. 10cc of conc H_2SO_4 (sp. gr. 1·83) is diluted with water so as to make 1 L of the soln. 20 cc of this soln require 28 cc of 0·25 N sodium carbonate soln. What was the percentage of acid in the conc sulphuric acid sample ? *West Bengal* H.S. *1974.*

Ans. 93·715.

20. *A laboratory bottle is labelled 12(N) HCl. How would you make from it 20cc of 3(N) HCl ? West Bengal* H. S. C. *1978.* Ans. Take 5cc acid and add 15cc dist. water.

21. 10cc of sulphuric acid (sp. gr = 1·85) were diluted with distilled water to one litre. 10cc of this soln required 34·65cc of decinormal NaOH soln for complete neutralisation. Calculate the percentage by wt of H_2SO_4 in the original acid. *Ranchi.* U. *1969.* Ans. 91·72.

22. 22cc of (N) H_2SO_4 neutralise 20·6cc KOH soln. How much water must be added to 1 litre of the latter to make it exactly N/2 ? *West Bengal J. E. E. 1971.* Ans. 1134cc or 1·134 litre.

23. 20cc of N/10 soln of NaOH require for its neutralisation 18·5cc of HCl soln. How much water must be added per litre of the above HCl soln to make it exactly decinormal ? *West Bengal J. E. E. 1973.* Ans. 80cc.

24. 20cc (N) hydrochloric acid is mixed with 60cc $\left(\frac{N}{2}\right)$ sulphuric acid. This mixture is neutralised with 0·33(N) caustic soda soln. How many cc of caustic soda will be required for neutralisation ? *West Bengal H.S. Tech. 1974.* Ans. 151·515cc.

25. 25cc of (N/10) HCl neutralise 22·5cc of NaOH soln. How much water must be added to 1 litre of the latter to make it exactly N/10 ? *West Bengal J. E.* E. *1978.* Ans. 100 cc.

26. A 0·50 gm sample of impure calcium carbonate is dissoved in 50 ml of 0·0985 (N) hydrochloric acid. After the reaction is complete, the excess hydrochloric acid requires 6·0 ml of 0·105 (N) caustic soda for neutralisation. Find the percentage of calcium carbonate in the sample. *I.I.T. (gp. A) 1971.* Ans. 43.

27. 10cc of HCl neutralise 40cc (N) NaOH. 1 gm of a sample of chalk is dissolved in another 10cc of the same acid and the excess acid required 20·5cc (N) NaOH for complete neutralisation. Calculate the percentage of $CaCO_3$ in the sample of chalk. *Ranchi. U. 1975.* Ans. 97·5.

28. 1 gm of an ordinary sample of lime stone dissolved in 16·6cc of 0·92 (N) hydrochloric acid soln leaving some sandy residue. Calculate the percentage of $CaCO_3$ in the sample. *Patna.* U. *1974A.* Ans. 76·36.

29. 0·2815 gm of a sample of lime stone is dissolved in 30cc (N) HNO_3. Unreacted acid is neutralised by 24·5cc (*N*) *N*aOH. Calculate the percentage of $CaCO_3$ in that sample. *West Bengal H.S. 1977.* Ans. 97·69.

30. A sample of impure calcium carbonate (containing an inert impurity) weighing 0·565 gm required 25cc of 0·404 (*N*) hydrochloric acid for exact neutralisation. Calculate the percentage purity of the impure sample of calcium carbonate. *West Bengal J. E. E.(Tc) 1978.* Ans. 89·38.

31. 4·2 gms of ammonium sulphate (pure) was treated with 100ml of sodium hydroxide soln (80 gms per litre) and the mixture heated to expel ammonia. It was cooled and diluted to 250 ml with distilled water. What volume of 0·2 (*N*) H_2SO_4 will be required to neutralise 25 ml of this soln ? *Ranchi.* U. *1971A.* Ans. 68·2 ml.

32. 7·5 gms of $(NH_4)_2SO_4$ were boiled with excess of NaOH soln and the evolved NH_3 was led into 50cc of (N) H_2SO_4, which finally required 8cc of N/2 NaOH for complete neutralisation. Calculate the % of N in $(NH_4)_2SO_4$. *Ranchi.* U. *1973S.* Ans. 8·58.

33. 2·871 gms of an ammonium salt are boiled with NaOH soln and the evolved ammonia is passed through 75cc (N) H_2SO_4. The unreacted acid requires 31·5 cc (N) NaOH for complete neutralisation. Find out the percentage of NH_3 in the ammonium salt. Magadh. U. 1975*S* Ans. 25·75.

34. A 10ml portion of $(NH_4)_2SO_4$ was treated with an excess of NaOH. The NH_3 gas evolved was absorbed in 50 ml of 0·1 (N) HCl. 10 ml of 0·2(N) NaOH was required to neutralise the remaining HCl. How many gms of $(NH_4)_2SO_4$ are in a litre of soln ? *I. I. T.* (gp. A) *1974.* Ans. 19·8 gms.

35. 1·524 gms of NH_4Cl were dissolved in water and 50cc(N) KOH soln were added to it. The total soln was boiled till NH_3 (g) ceased to be evolved and was then neutralised with 30·95cc (N) H_2SO_4 soln. Calculate the % of NH_3 in the sample of NH_4Cl. *Ranchi.* U. 1976. Ans. 21·25.

36. 2·26 gms of an ammonium salt were boiled with 50ml of normal caustic soda soln until all ammonia had been expelled. The soln then required 20ml of seminormal sulphuric acid for neutralisation. Find the percentage of NH_3 in the ammonium salt. *Bhagalpur.* U. 1976. Ans. 30·08.

37. 5·6 litres of dry ammonia gas at S.T.P is passed through 1 lit of (N)H_2SO_4. What volume of 0·1(N) KOH will be required to neutralise the mixture ? [If necessary, you may use S=32 and N=14] *West Bengal* H. S. C. 1978. Ans. 7·5 lits.

38. 2 gms of a mixture of HH_4Cl and NaCl are heated with 50cc of (N) NaOH until all ammonia has been driven off. The excess of alkali present is then neutralised with 20cc (N) H_2SO_4. Determine the percentage of NH_4Cl in the mixture.

Bombay. U. *I. Sc.* 1977. Ans. 80·25.

39. Find out the volume in ml of 0·1 (N) hydrochloric acid required to react completely with 1 gm of a mixture of sodium carbonate and sodium bi carbonate containing equimolar amounts of the two compounds. *I. I. T. 1971.* Ans. 157·9ml.

40. 2·1 gms of a mixture of $NaHCO_3$ and $KClO_3$ require 100ml of 0·1 (N) HCl for complete reaction. Calculate the amount of residue that would be obtained on strongly heating 2·2 gms of the same mixture. *I.I.T. 1972.* Ans. 1·328 gms.

41. 3·4914 gms of a mixture of NaOH and KOH are dissolved in water and diluted to 250cc. 10cc of this diluted soln required 13·6cc of 0·25 (N) acid for complete neutralisation. What is the percentage of KOH in the mixture ? *Ranchi.* U. *1972.* Ans. 9·3.

42. 2·5 gms of a mixture of $CaCO_3$ and $MgCO_3$ was

dissolved in 80cc of 1·05 (N) HCl. The soln was then diluted to 250cc. 25cc of this soln required 30·2cc of N/10 NaOH for complete neutralisation. Calculate the percentage composition of the mixture. *Ranchi.* U. *1974*A. Ans. 60% $CaCO_3$; 40% Mg CO_3.

43. 10 gms of soda crystals ($Na_2CO_3, 10H_2O$) are required to neutralise 50cc of a sample of HCl soln. How many cc of this acid must be diluted and made up to one litre so as to produce exactly (N) HCl soln? *Magadh.* U. *1972.* Ans. 715 cc.

44. 3·35 gms of hydrated sodium carbonate were dissolved in 200cc of water. 50cc of this soln required 58·50cc of N/10 H_2SO_4 for complete neutralisation. Calculate the number of molecules of water of crystallisation in one molecule of hydrated sodium carbonate. *Ranchi.* U. *1973.* Ans. 10.

45. 1·215 gm of a sample of $CuSO_4, XH_2O$ was dissolved in water. H_2S, passed till CuS was completely precipitated. The filtrate contained liberated H_2SO_4 which required 20 ml of N/2 NaOH for complete neutralisation. Calculate X, the number of molecules of water associated with $CuSO_4$.

U. *P. Board. I.Sc. 1972.* Ans. 5.

46. 3·12 gms of washing soda (Na_2CO_3, $10H_2O$) crystals were dissolved in 200 cc of water. 20 cc of the resulting soln, titrated with N/10 H_2SO_4 required 21·8cc for exact neutralisation. Calculate the percentage of anhydrous Na_2CO_3 in the crystals.

Ranchi. U. *1974.* Ans. 37·02.

47. 10 cc of 1 (N) sodium carbonate soln require 5 cc of 1 (N) hydrochloric acid soln for neutralisation if phenolphthalein be used as indicator. Explain why? *West Bengal H.S.C. 1978.*

Ans. See solved problem No. 22.

48. An aqueous soln containing 0·475 gm of a mixture of Na_2CO_3 and $NaHCO_3$ was titrated with 0·5 (N) H_2SO_4 soln using methyl orange as indicator. The volume of 0·5 (N) H_2SO_4

soln required was 15 ml for the end point. Calculate the percentage of Na_2CO_3 in the mixture.

Calcutta. U. B. Sc. *1970*. Ans. 57·263.

49. An alkaline soln contains both NaOH and Na_2CO_3. 20cc of this soln require for neutralisation 30cc of N/10 HCl, when phenolphthalein is used as an indicator. But on adding methyl orange, the soln is found to be alkaline even now and requires 10cc more of the same acid for complete neutralisation. Calculate the weights of NaOH and Na_2CO_3 in one litre of the alkaline soln. Ans. 5·3 gm Na_2CO_3 ; 4 gm NaOH.

50. Calculate the volume in ml of semi normal hydrochloric acid required to precipitate 71·75 gms of AgCl from $AgNO_3$ soln. (Ag = 108 ; Cl = 35·5). *Patna*. U. *1970 A*. Ans. 1 litre.

51. Calculate the amount of NaCl in gms necessary for complete precipitation of Ag^+ from 41·05 ml of M/10 $AgNO_3$ soln. *Calcutta*. U. B. Sc. *1970*. Ans. 0·24 gm.

52. Calculate the amount of NaCl necessary for complete precipitation of silver ion present in 50 ml of M/10 silvernitrate soln. *Calcutta*. U. B. Sc. *1976*. Ans. 0·7925 gm.

53. 50 cc of a soln of copper sulphate was boiled with 50 cc (N) NaOH soln and filtered. The residue was thoroughly washed to remove all the alkali. The excess of NaOH present in the filtrate and washing required 250 cc N/10 H_2SO_4 for complete neutralisation. Calculate the amount of $CuSO_4$ present in 500 cc of the original soln. *Bihar*. U. *1971A*. Ans. 93·74 gms.

54. 20 cc of a soln containing H_2SO_4 and HCl required 30 cc of 0·5 (N) NaOH soln for complete neutralisation. 10 cc of acid soln when treated with $AgNO_3$ gave 0·4305 gm of AgCl. Find the weights of H_2SO_4 and HCl in a litre of the acid soln. *Ranchi*. U. *1968 A, 1975S*. Ans. $H_2SO_4 = 22·05$ gms ; HCl = 10·95 gms.

55. 10 cc of a soln of HCl exactly neutralise 15 cc of a soln of NaOH. Also 10 cc of the same HCl soln when treated with

excess of $AgNO_3$ soln give 0·1435 gm of AgCl. Find out the strength of NaOH soln in gm/litre. *West Bengal J. E. E. 1975* ; *Calcutta*. U. B. Sc. *1976*. Ans. 0·066 (N).

56. (i) A soln of a mixture of KCl and KOH was neutralised 120 ml of 0·12 N HCl. Calculate the amount of KOH in the mixture. (ii) After titration, the resultant soln was made acidic with HNO_3. Then excess of $AgNO_3$ soln was added to precipitate AgCl which weighed 3·7 gms after drying. Calculate the percentage of KOH in the original mixture.

I. I. T. 1973. Ans. 0·8064 gm ; 48·74%.

57. To 10 cc of a soln of $CaCl_2$ was added 20 cc of (N) Na_2CO_3 soln and the mixture was warmed. The precipitate was removed by filtration and washed. The total filtrate and washings were then diluted to 250 cc. 10 cc of this diluted soln required 1·6 cc of N/4 HCl for complete neutralisation. Calculate the strength of $CaCl_2$ soln in gms of $CaCl_2$ dissolved per litre (Ca = 40 ; Cl = 35·5). *Ranchi*. U. *1970*. Ans. 55·5.

58. A mixture containing only Na_2CO_3 and K_2CO_3 weighing 1·22 gm was dissolved in water to form 100 ml of a soln. 20 ml of this soln required 40 ml of 0·1 (N) HCl for neutralisation. Calculate the weight of Na_2CO_3 in the mixture. If another 20 ml portion of the soln is treated with excess $BaCl_2$, what will be the weight of the precipitate thus obtained ?

I. I. T. (*gp A.*) *1976*. Ans. 0·3946 gm.

59. 2 gms of the carbonate of a metal were dissolved in 50 cc of (N) HCl. The resulting liquid required 100 cc of N/10 NaOH soln to neutralise it completely. Calculate the equivalent weight of the metal. *West Bengal J.E.E. 1969*. Ans. 20.

60. 0·23 gm of the oxide of a metal M required for complete neutralisation 15 cc of N/5 HCl. Carbonate of the metal had the formula MCO_3. What is the at wt of the metal ?

Bihar University ; *Ranchi. U. 1969*. Ans. 137·2.

61. 1 gm of MCO_3 was dissolved in 50 ml (N) HCl. The

remaining acid required 30 ml of (N) NaOH for complete neutralisation. Find the equivalent weight of MCO_3 and from it deduce the atomic weight of M.

L. N. M. U. *1975 A.* Ans. 50 ; 40.

62. 1·2 gm of a pure alkali is dissolved in 250 ml distilled water. 25 ml of this soln require 30 ml (N) HCl for neutralisation. Calculate the equivalent weight of the alkali.

L. N. M. U. *1976 A.* Ans. 4.

63. Calculate the number of sodium ions in one litre of 1 (M) sodium sulphate solution. *Indian School Certificate Examination. 1978.* Ans. 2.

64. Calculate the mass of copper deposited when an excess of zinc is added to 100 cm^3 of a solution containing 249·5 gms of $CuSO_4 . 5H_2O$ perlitre. *Indian S. C.E. 1978.* Ans. 63·5 gms.

65. 1 gm of pure NaOH is dissolved in water and 15 cc of (N) H_2SO_4 are added. Is the solution acidic or alkaline ? Give reasons. [Na = 23] W. *B. J. E. E. 1977* & 1980. Ans. alkaline.

66. 20 cc of N/2 HCl, 50 cc of N/5 HNO_3 and 80 cc of N/10 H_2SO_4 were mixed together. Find the normality of the resulting mixture. W.*B.J.E.E.* 1977. Ans. 0·18 (N).

67. 18 ml N/2 HCl is mixed with 20·6 ml 2N HCl and 16·4 ml N/10 HCl. 30 ml of this mixture is diluted to 250 ml. What would be the volume of (0·905) N/10 Na_2CO_3 solution required to neutralise 20 ml of this diluted solution ?

Ranchi. U. *1978.* Ans. 24·97 ml.

68. A bottle of commercial sulphuric acid is labelled 86% by wt of sulphuric acid. Its density is 1·787 g/cc. What is the molarity of the acid solution ? W. *B. H. S. C.* & *I. I. T. 1979.* What volume of the acid has to be used to make 1 litre of 0·2M H_2SO_4 ? Ans. 8·43(M), 23 lit.

69. Two grams of a sample of ammonium chloride contaminated with sodium chloride is mixed with 50 ml of N NaOH solution and the solution is boiled till there is no change of colour of a moist red litmus paper held in the vapour. The

solution after cooling requires 20ml of NH_2SO_4 for neutralisation. What was the percentage of ammonium chloride in the sample?
W.B. H. S. C. 1979. Ans. 19·75.

70. 5·5g of a mixture of $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.9H_2O$ require 5·4 ml of 0·1 N$KMnO_4$ solution for completeoxidation. Calculate the number of gm moles of hydrated ferric sulphate in the mixture. *I. I. T. 1979.* [Hint. 5·4 ml of 0·1 N $KMnO_4 \equiv$ 0·00054 gm eq $FeSO_4$, $7H_2O$. ∵ eq. wt of $FeSO_4.7H_2O=278$ ∴ wt of $FeSO_4$, $7H_2O=0{\cdot}15$ gm ; wt of $Fe_2(SO_4)_3.9H_2O$ $=5{\cdot}35$ gm $=0{\cdot}0095$ gm mole. Mol. wt of $Fe_2(SO_4)_3.9H_2O=562{\cdot}1$. ∵ S = 32·1]

71. A solution contains Na_2CO_3 and $NaHCO_3$. 10 ml of the solution require 2·5 ml of 0·1 M H_2SO_4 for neutralisation using phenolphthalein as an indicator. Methyl orange is then added when a further 2·5 ml of 0·2M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in one litre of the solution.
I. I. T. 1979.

[Hints. Amount of Na_2CO_3 in 10 ml soln ≡ 5ml 0·2 (N) $H_2SO_4 \equiv$ 5ml 0·2 (N) Na_2CO_3. 1000 ml (N) Na_2CO_3 soln contain 53 gms. ∴ 5 ml 0·2 (N) Na_2CO_3 soln contain 0·053 gm. 10ml soln contain 0·053 gm Na_2CO_3 ∴ amount of Na_2CO_3/litre = 5·3 gms. Amount of $NaHCO_3$ in 10 ml soln ≡ (5 − 2·5) ml of 0·2 (N) $H_2SO_4 \equiv$ 2·5 ml of 0·2 (N) $NaHCO_3$. 1000 ml (N) $NaHCO_3$ contain 84 gm ∴ 2·5 ml 0·2 (N) $NaHCO_3$ soln contain 0·042 gm. 10ml soln. contain 0·042gm $NaHCO_3$ ∴ amount of $NaHCO_3$/litre = 4·2 gms.]

72. 0·01 gm atom of zinc metal was completely dissolved in 90·5cc of dil. sulphuric acid soln. The resulting soln still required exactly 17·5cc of 0·15 (N) caustic soda soln for complete neutralisation. Calculate the normality of the acid and the weight of zinc sulphate formed. *W. B. J. E.E. 1979.*

[Hint. $Zn+H_2SO_4 \rightarrow ZnSO_4+H_2$
65·38 gm 2000cc (N) 161·38 gm
0·01 × 65·38 gm 20cc (N) 1·6138 gm.

Volume of sulphuric acid used = 20cc (N) H_2SO_4 and vol of acid unused = 17·5cc of 0·15 (N) H_2SO_4 = 2·625cc (N) H_2SO_4. Total vol of acid = 22·625cc (N) H_2SO_4

$\therefore$ 22·625 × (N) = 90·5 × S $\therefore$ S = 0·25 (N).]

73. 100ml of a dil. solution of hydrochloric acid was completely neutralised with 200 ml of a dil. solution of sodium hydroxide. The neutralised soln on evaporation gave 5·85 gms of solid residue. Calculate the strengths of the hydrochloric acid and sodium hydroxide solns, respectively, in terms of normality. *W. B. J. E. E. (Tc) 1979.*

[Hints. $HCl + NaOH \rightarrow NaCl + H_2O$

36·5 gm HCl react with 40 gm NaOH to form 58·5 gm NaCl (solid residue)

Or, 3·65 „ „ „ „ 4 „ „ „ 5·85 „

$\therefore$ strength of $HCl = \frac{3·65}{100} \times \frac{1000}{36·5}$

$= 1$ (N) and strength of $NaOH = \frac{4}{200} \times \frac{1000}{40} = \frac{1}{2}$ (N).]

74. An organic monobasic acid gives the following combustion data : 0·100 gm gave 0·2525 gm of CO_2 and 0·0432 gm of H_2O. 0·122 gm of the acid required 10 ml of N/10 barium hydroxide solution for neutralization. What is the constitutional formula of the acid? *W. B. J. E. E. 1979.* Ans. $C_7H_6O_2$; C_6H_5COOH.

75. 1·64 gms of a mixture of calcium carbonate and magnesium carbonate were dissolved in 50 cc of 0·8 N hydrochloric acid. The excess (unused) of the acid required 16 cc N/4 sodium hydroxide solution for neutralisation. Find out the percentage composition of mixture of the two substances.

P.M.T. Meerut 1970. Ans. 43·5% $CaCO_3$; 56·5% Mg CO_3.

76. How much silver chloride will be formed by adding 200 ml of 5 *N* hydrochloric acid to a solution containing 1·7 gms of silver nitrate? *Uttar Pradesh I. Sc. 1970.* Ans. 1·435 gms.

77. 40 ml of HCl is exactly neutralised by 20 ml of NaOH

soln. The resulting neutral soln is evaporated to dryness and the residue is found to have a mass of 0·117 gm. Calculate the normality of HCl and NaOH solns.

Uttar Pradesh I. Sc. 1977. Ans. N/20, N/10.

78. 0·1435 gm of AgCl is obtained from 20 ml HCl. Determine th normality of the acid. U. *Pradesh* 1977S. Ans. N/20.

79. Find out the volume of hydrogen which would be evolved at N. T. P. by reacting zinc with 50 ml of 40% pure dil. H_2SO_4 whose sp. gravity is 1·3. [Zn=63·5] U. *P. 1978.* Ans. 5942·8 ml.

80. 2·65 gms of a diacidic base was dissolved in water and made upto 500 ml. 20 ml of this soln completely neutralise 12 ml of N/6 HCl. Find out the equivalent weight and molecular weight of the base. *U. P.* 1978. Ans. 53 ; 106.

81. In a sample of Na_2CO_3 some Na_2SO_4 is mixed. 1·25 g of this sample is dissolved and the volume made upto 250 ml. 25 ml of this soln neutralises 20 ml $N/10$ H_2SO_4. Calculate the percentage of Na_2CO_3 in the sample.

U.P. 1978S. Ans. 84·8%.

82. A piece of Al weighing 2·7 gm is treated with 75 ml H_2SO_4 (sp. gr. 1·18, containing 24·7% H_2SO_4 by wt.). After the metal is completely dissolved the soln is diluted to 400 ml. Calculate the molarity of the H_2SO_4 in the resulting soln ?

Roorkee Adn. T. E. 1977. Ans. 0·183.

83. A polyvalent metal weighing 0·1 gm and having at. wt. 51 reacted with dil. H_2SO_4 to give 43·9 ml H_2 at N.T.P. The soln containing the metal this lower oxidation state, was found to require 58·5 ml of 0·1 N permanganate for complete oxidation. What are valencies of the metal ? *I.I.T. 1977.* Ans. 2 ; 3.

84. A sample of magnesium metal containing some magnesium oxide as impurity was dissolved in 125 ml 0·1 N H_2SO_4. The vol of H_2 evolved at 27·3°C and latm. was 120·1 ml. The resulting soln was found to be 0·02 N with respect to H_2SO_4. Calculate (i) the weight of the sample dissolved and (ii) the

percentage by weight of magnesium in the sample. Neglect any change in the vol of the soln. *I.I.T. Adn. T.E. 1977*. Ans. 0·1236g ; 95·15%.

85. 7·45 gm of KCl are dissolved in 250 ml of water. Calculate the molarity of the solution. *Uttar Pradesh I.Sc. 1976.* Ans. 0·4.

86. 1·325 gms of anhydrous sodium carbonate were dissolved in water and the soln was made upto 250 ml. Calculate the normality of the soln. U*ttar Pradesh I. Sc.* 1978 S. Ans. N/10.

87. 20 cc of N/2 NaOH soln is added to 30 cc *N*/5 HCl soln. How will the resulting soln react with litmus.
Ravisankar U. *B. Sc.* 1977 Ans. alkaline.

88. (a) What amounts of Na_2CO_3 will be required to prepare the following solutions ? (i) 250 cc. 0·5N Na_2CO_3 ; (ii) 500 cc 0·5M Na_2CO_3 and (iii) 1000cc 5% Na_2CO_3 (Na=23). (b) 25cc of a 0·1N NaOH solution neutralises 22·5 cc of a HCl soln. How much water is to be added to 500 cc of the HCl soln to make it 0·1N ? *W. B. H. S. C. 1980*. Ans. (i) 6·625 gms, (ii) 26·5 gms (iii) 50 gms (b) 55·5 cc.

89. (a) One litre of a sample of hard water contains 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$. Find the total hardness in terms of parts of $CaCO_3$ per 10^6 parts of water by weight. (b) A sample of hard water contains 20 mg of Ca^{++}ions per litre. How many milli equivalents of Na_2CO_3 would be required to soften 1 litre of the sample ? (c) 1 gm of Mg is burnt in a closed vessel which contains 0·5 gm of O_2. (i) Which reactant is left in excess ? (ii) Find the weight of the excess reactant. (iii) How many millilitres of 0·5 NH_2SO_4 will dissolve the residue in the vessel ? *I. I. T. 1980.*

[Hints : (a) $1 \text{ mg } CaCl_2 \equiv \frac{10^{-3}}{55·5}$ gm. eq. Ca^{++} ; 1 mg $MgCl_2$

$=\frac{10^{-3}}{47·5}$ gm. eq. Mg^{++}.

$\therefore \frac{10^{-3}}{55·5}+\frac{10^{-3}}{47·5}$ gm. eq. Ca^{++} and $Mg^{++}=0·039\times10^{-3}$ gm. eq.

Ca^{++} and $Mg^{++} \equiv 0{\cdot}039 \times 10^{-3}$ gm. eq. $Ca^{++} \equiv 0{\cdot}039 \times 10^{-3}$ gm. eq. $CaCO_3$ by law of equivalent proportion. 1000 cc (1 litre) $= 10^3$ gm water contain $0{\cdot}039 \times 10^{-3}$ gm. eq. $CaCO_3 = 0{\cdot}039 \times 10^{-3} \times 50$ gm $CaCO_3$ ∴ 10^6 gm water contain $0{\cdot}039 \times 10^{-3} \times 50 \times 10^3$ gm $CaCO_3 = 1{\cdot}95$ gm $CaCO_3$. (b) 20 mg $Ca\ ^{+}$/litre $\equiv \frac{20 \times 10^{-3}}{20}$ gm. eq. Ca^{++}/litre $= 10^{-3}$ gm. eq. Ca^{++}/litre $\equiv 10^{-3}$ gm. eq. Na_2CO_3/litre $= 10^{-3} \times 10^3$ milli gm.eq. Na_2CO_3/litre $= 1$ milli eq. Na_2CO_3/litre. (c) Ans. (i) Mg., (ii) 0·25 gm., (iii) 41·66 ml 0·5(N)H_2SO_4.]

90. (a) (i) A sample of $MnSO_4.4H_2O$ is strongly heated in air. The residue is Mn_3O_4. (ii) The residue is dissolved in 100 ml of 0·1N$FeSO_4$ containing dilute H_2SO_4. (iii) The solution reacts completely with 50 ml of $KMnO_4$ solution. (iv) 25 ml of the $KMnO_4$ solution used in step (iii) requires 30 ml of 0·1N $FeSO_4$ solution for complete reaction. Find the amount of $MnSO_4.4H_2O$ present in the sample. (b) 0·5 gm of fuming H_2SO_4 (oleum) is diluted with water. This solution is completely neutralised by 26·7 ml of 0·4N NaOH. Find the percentage of free SO_3 in the sample of oleum. (c) Find the equivalent weight of H_3PO_4 in the reaction : $Ca(OH)_2 + H_3PO_4 = CaHPO_4 + 2H_2O$. *I. I. T.* 1980.

[Hints : $30 \times 0{\cdot}1(N) = 25 \times$ strength of $KMnO_4$ ∴ strength of $KMnO_4 = 0{\cdot}12(N)$. 50 ml $0{\cdot}12(N)KMnO_4 \equiv 50$ ml $0{\cdot}12(N)$ $FeSO_4$ soln $\equiv \frac{50 \times 0{\cdot}12}{0{\cdot}1}$ ml $0{\cdot}1(N)FeSO_4$ soln $= 60$ ml $0{\cdot}1\ (N)FeSO_4$ soln. ∴ $(100-60)$ ml $= 40$ ml $0{\cdot}1(N)FeSO_4$ soln used to dissolve $Mn_3O_4 \equiv \frac{40 \times 0{\cdot}1}{1000}$ gm. eq. $Fe^{++} = \frac{4}{1000}$ gm. eq. $Fe^{++} \equiv \frac{4}{1000}$ gm. eq. $Mn_3O_4 \equiv \frac{4}{1000}$ gm. eq. $MnSO_4.4H_2O = \frac{4}{1000} \times 111{\cdot}5$ gm

$MnSO_4.4H_2O = 0{\cdot}446$ gm. $MnSO_4.4H_2O$.

(b) 26·7 ml 0·4(N)NaOH $\equiv$ 26·7 ml 0·4(N)H_2SO_4

$= \frac{26{\cdot}7 \times 0{\cdot}4}{1000} \times 49 = 0{\cdot}011$ gm H_2SO_4.

∴ amount of SO_3 in the sample of oleum $=(0\cdot5-0\cdot011)$ gm $=0\cdot489$ gm. % of free SO_3 in the sample of oleum

$$=\frac{0\cdot489}{0\cdot5}\times100=\frac{48\cdot9}{0\cdot5}=97\cdot8.$$

(c) Ans. 49.

91. 0·7 gm of an organic compound was analysed by Kjeldahl's method, the NH_3 produced was absorbed in 100 ml of N/10 H_2SO_4. The excess acid required 10 ml of *N*/5 NaOH for neutralization. Calculate the precentage of nitrogen in the compound. U. *P*. 1977. Ans. 16.

92. 0·45 gm of an organic compound on ignition gave 0·792 gm CO_2 and 0·324 gm water. By Kjeldahl's method 0·24 gm of the substance yielded NH_3, which was dissolved in *25* ml of *N*/2 H_2SO_4. The excess of H_2SO_4 was neutralised with 38·5ml of *N/5* NaOH solution. Calculate the percentage of C, H and *N* in the compound.

U*ttar Pradesh I. Sc. 19*78. Ans. $\%C=48$, $\%H=8$, $\%N=28$.

93. What will be normality of 0·I M soln of $KMnO_4$, when it is used as an oxidant in acidic medium ?

Ravisankar U. (*B.Sc.*) 1978. Ans. 0·5(*N*).

94. HCl of sp. gravity 1·*25* contains 50% pure HCl by weight. How much volume of this HCl will be required to prepare NHCl in one litre ?

Ravisanker U. B. Sc. 1973, 1975. Ans. 0·0876 lit.

95. Find out the concentration of an oxalic acid solution in gms of anhydrous acid per litre, *20* cc of which require 15 cc of *N/25* pot. permanganate soln (Eq. wt of anhydrous oxalic acid=45) *Ravisankar* U. *B. Sc. 1974.* Ans. 1·35 gm.

96. 0·225 gm. oxalic acid required 50 ml 0·1 N pot. permanganate soln for complete oxidn. What is the eq. wt. of oxalic acid ?

Ravisankar U. *B. Sc. 1976.* Ans. 45.

97. 1 gm. of a pure sample of metal dissolves completely in 100cc NHCl soln. The excess of acid was neutralised with 16·7 cc N NaOH soln. The sp. heat of the metal is 0·27. Find out the correct at. wt. of the metal. *Ranchi* U. *1979*. *Ans. 24.*

CHAPTER 11

Problems on electrolysis, "solubility and solubility product" and PH.

Electrolysis :

An electrolyte conducts electricity in its fused state or in its aqueous solution by virtue of the movement of ions. Such electrolytes are decomposed by the passage of electric current. The products of this decomposition are obtained by removal or addition of electrons. The decomposition of an electrolyte by passing an electric current is called electrolysis.

Faraday's laws of electrolysis :

Ist law : The law states that, "The weight of an element liberated at a given electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte". Mathematically, it can be stated as, $W \propto Q \propto c.t.$

$\therefore$ $W = z.c.t.$ Where, W = wt of the element in gms ; c = current strength in amp ; t = time in second. Q = quantity of electricity in coulomb and z = electro chemical equivalent, the constant of proportionality. When, c = lampere and t = 1 second ; $Q = ct = 1 \times 1 = 1$ coulomb. $W = z.\ c.\ t = z.\ 1.\ 1 = z.$ Thus, electro-chemical equivalent of an element is the weight of the element that is liberated by the passage of 1 coulomb of electricity through the electrolyte.

2nd law : The law states that, "When the same quantity of electricity is passed through different electrolytes, the weights of different ions liberated at the different electrodes are in the ratio of their chemical equivalents.

$$\text{Thus, } \frac{\text{Weight of ion 'X'}}{\text{Weight of ion 'Y'}} = \frac{\text{Chemical equivalent of X}}{\text{Chemical equivalent of Y}}$$

It is noted by experiments that 96500 coulombs of electricity are needed to liberate 1 gm equivalent weight of any element. This quantity of electricity is called one Faraday.

One Faraday (F) = 96,500 coulombs = 1 gm equivalent weight of element. The minimum quantity of electricity carried by either a singly charged positive ion or a negatively charged ion is found out by the following relation : $e=\frac{F}{N}$, where, e = minimum quantity of electricity, F = faraday of electricity and N = avogadro's number $=6{\cdot}023\times10^{23}$. Unit of e is then coulomb.

From Ist and 2nd law of Faraday we can write,

$$\frac{\text{Chemical equivalent of X}}{\text{Chemical equivalent of Y}}=\frac{\text{Electro chemical eq. of X}}{\text{Electro chemical eq. of Y}}.$$

Solubility and solubility product

Solubility : The solubility of a solid in a solvent (liquid) at a given temperature is the number of gms of the solid (solute) which dissolves in 100 gms of the solvent to give a saturated solution at that temperature.

Let a gm of a solute saturate b gm of a solvent at t°C, then its solubility at $t^\circ C=\frac{100\times a}{b}$. If A gms of a solute be present in B gms of its saturated soln at t°C, then its solubility at t°C $=\frac{100\times A}{B-A}$.

Solubility product : A little of a sparinghy soluble strong electrolyte (e.g., AgCl) is shaken with distilled water in a reagent bottle at a definite temperature, a state of equilibrium is reached following the reversible reaction,

$AgCl\ (solid) \rightleftharpoons AgCl\ (soln) \rightleftharpoons Ag^+ + Cl^-$.

Since, silver chloride (AgCl) is a strong electrolyte, the dissolved portion of the electrolyte AgCl is totally ionised and an ionic equilibrium is established between solid silver chloride and silver and chloride ions at the definite temperature. On applying the law of mass action to the equilibrium reaction, we get, $K=\frac{[Ag^+]\,[Cl^-]}{[AgCl\ (Solid)]}$ or $K\,[AgCl\ (Solid)]=[Ag^+]\,[Cl^-]$.

Where, K is the ionisation constant. Since, concentration of any solid substance in a saturated solution at definite temperature is constant, we have, $Ks=[Ag^+][Cl^-]$. Where, Ks is a constant, known as the *solubility product* of silver chloride. Considering ionisation of a sparingly soluble strong electrolyte A_mB_n, we get, $A_mB_n \rightleftharpoons mA^+ + nB^-$, then $K=[A^+]^m[B^-]^n$ at the definite temperature. *Solubility product* of an electrolyte is therefore defined as the maximum product of concentrations of its constituent ions in its saturated solution at definite temperature, the power of each concentration term being raised to a number representing the number of ions of each type formed by the reversible ionisation of one molecule of the electrolyte. If S is the solubility of AgCl in moles/litre. Then, $K=[Ag^+][Cl^-]=S^2$. $\therefore S=\sqrt{K_s}$.

Solubility in gm moles= $\sqrt{\text{solubility product}}$; solubility in gms= $\sqrt{\text{solubility product}}\times$ molecular weight of the electrolyte.

Hydrogen ion concentration (PH – value) **:**

The concentration of H^+ i. e., $[H^+]$ can be conveniently expressed in the form of PH. The PH of a solution is the negative logarithm (to the base 10) of the effective concentration of hydrogen ion. $PH=-\log_{10}[H^+]$ and $PH+POH=14$. Where, $POH=-\log_{10}[OH^-]$.

Solved problems: *Electrolysis.*

1. For how long a current of 4 amperes is to be passed through 1 litre of a 1·2 molar copper sulphate solution to produce 10 gms of copper? (Cu=63; 1 Faraday=96,500 coulombs). *West Bengal H.S. 1974.*

1000 cc (1 litre) copper sulphate solution contain 1·2 gm mole $CuSO_4$.

or „ „ „ „ „ „ $(1·2\times\text{mol.wt of }CuSO_4)$gm „

or „ „ „ „ „ „ $(1·2\times\text{valency}\times\text{eq.wt})$ gm „

or „ „ „ „ „ „ $(1·2\times2\times\text{eq.wt})$ gm „

or „ „ „ „ „ „ $1·2\times2$ gm equivalent $CuSO_4$.

or $1{\cdot}2\times2$ gm equivalent copper is deposited at the electrode by $1{\cdot}2\times2\times96500$ coulombs of electricity. ∵ 96500 coulombs of electricity liberate 1 gm equivalent metal from 1 gm equivalent of its salt.

or $1{\cdot}2\times2\times\frac{63}{2}$ gm copper is deposited at the electrode by

$1{\cdot}2\times2\times96500$ coulombs of electricity

or 10 gm „ „ „ „ „ „

$$\frac{1{\cdot}2\times2\times96500\times10}{1{\cdot}2\times63}=30634{\cdot}92 \text{ „ .}$$

Now, $Q=ct$. Where, Q = quantity of electricity in coulombs ; c = current strength in amperes and t = time in seconds.

or $30634{\cdot}92=4\times t$ ∴ $t=\frac{30634{\cdot}92}{4}=7658{\cdot}73$ seconds.

2. A current of 1·5 amperes is passed through 40 litres of 1·2 molar copper sulphate solution for two hours. Calculate the weight of products discharged at electrodes and the strength of the acid produced in terms of normality. (1 Faraday = 96,500 coulombs ; Cu = 63·6) *West Bengal H. S. 1973.*

1 litre copper sulphate solution contains 1·2 gm mole $CuSO_4$.

40 litres of copper sulphate solution contain $1{\cdot}2\times40$ gm mole $CuSO_4$.

or „ „ „ „ „ „ $1{\cdot}2\times40\times2$ gm eq $CuSO_4$.

or, $1{\cdot}2\times40\times2$ gm eq copper is deposited at the electrode by $1{\cdot}2\times40\times2\times96500$ coulombs of electricity.

or, $1{\cdot}2\times80\times96500$ coulombs of electricity liberate

$$\frac{1{\cdot}2\times80\times63{\cdot}6}{2} \text{ gm Cu.}$$

∴ $1{\cdot}5\times2\times60\times60$ „ „ „ „

$$\frac{1{\cdot}2\times80\times63{\cdot}6\times1{\cdot}5\times2\times60\times60}{2\times1{\cdot}2\times80\times96500} \text{ gm Cu.}$$

$$=3{\cdot}558 \text{ gm copper.}$$

Now, 3·558 gm copper $=\frac{3{\cdot}558}{\frac{63{\cdot}6}{2}}$ gm eq copper $=0{\cdot}1118$ gm eq copper.

$\equiv 0{\cdot}1118$ gm eq sulphate $\equiv 0{\cdot}1118$ gm eq sulphuric acid.

40 litre solution contain 0·1118 gm eq sulphuric acid after electrolysis.

$\therefore$ 1 „ „ contains $\frac{0{\cdot}1118}{40} = 0{\cdot}00279$ „ „ „ „ .

Strength of the acid produced $= 0{\cdot}00279$ (N) ; 0·1118 gm eq sulphate obtained is converted into sulphuric acid $= 0{\cdot}1118 \times 48 = 5{\cdot}366$ gms. $\because$ equivalent weight of sulphate $= 48$.

3. A current of 0·75 amp is passed for 45 minutes through a metallic salt solution and the cathode was found to have gained in weight by 0·6662 gm. What is the equivalent weight of the metal ? *W. B. H. S. C.* 1980.

$0{\cdot}75 \times 45 \times 60$ coulombs of elecsrricity deposit 0·6662 gm metal

$\therefore$ 96500 „ „ „ „ $\frac{0{\cdot}6662 \times 96500}{0{\cdot}75 \times 45 \times 60}$

$= 31{\cdot}747$ „

$\therefore$ equivalent weight of the metal $= 31{\cdot}747$.

4. 19 gm of molten $SnCl_2$ is electrolysed for sometime. Inert electrodes are used. 0·119 gm of Sn is deposited at the cathode. No substance is lost during the electrolysis. Find the ratio of the weights of $SnCl_2 : SnCl_4$ after electrolysis.

I. I. T. 1980. [Sn = 119]

0·119 gm of Sn $\equiv \frac{0{\cdot}119}{59{\cdot}5}$ gm. eq. $Sn^{++} = 0{\cdot}002$ gm eq Sn^{++}

$\equiv 0{\cdot}002$ gm eq $Cl^- \equiv 0{\cdot}002$ gm eq $SnCl_4$

[$\because$ $Sn^{++} - 2e \rightarrow Sn^{++++}$; $Sn^{++++} + 4Cl^- \rightarrow SnCl_4$.]

$= \frac{0{\cdot}002 \times 261}{4} = 0{\cdot}1305$ gm $SnCl_4$ after electrolysis. Now, 19 gm $SnCl_2 \equiv \frac{19}{95}$ gm. eq $SnCl_2 = 0{\cdot}200$ gm eq. $SnCl_2$ = amount of $SnCl_2$ before electrolysis. Amount of $SnCl_2$ electrolysed $= 0{\cdot}002$ gm eq.

$\therefore$ after electrolysis, amount of $SnCl_2 = (0{\cdot}200 - 0{\cdot}002)$ gm.eq.

$= 0{\cdot}198$ gm. eq. $= \frac{0{\cdot}198 \times 190}{2} = 18{\cdot}81$ gm.

The ratio of the weights of $SnCl_2 : SnCl_4$ after electrolysis

$=\frac{18{\cdot}81}{0{\cdot}1305}$ i.e. ; 18·81 : 0·1305.

5. How much current is to be required to deposit 10 gm iodine from potassium iodide solution in 1 hr ?

Magadh. U. 1976A.

96500 coulombs of electricity is required to deposit 1 gm eq iodine.

or, ,, ,, ,, ,, ,, ,, ,, ,, 127 gm ,,

∴ C×60×60 ,, ,, ,, ,, ,, ,, $\frac{127 \times C \times 60 \times 60}{96500}$ gm ,,.

According to the question, $\frac{127 \times C \times 60 \times 60}{96500} = 10.$

Where, C = current strength in amps.

∴ C = 2·11 amperes [eq wt of iodine = 127].

6. A solution of a salt of a metal of at wt 112 was electrolysed for 90 minutes with a current 0·15 ampere. The weight of the metal deposited at the cathode was 0·4698 gm. Find the valency of the metal in the salt.

West Bengal H. S. 1977.

90×60×0·15 coulombs of electricity is required to deposit 0·4698 gm metal

∴ 96500 ,, ,, ,, ,, ,, $\frac{0{\cdot}4698 \times 96500}{90 \times 60 \times 0{\cdot}15}$

= 55·97 gm metal.

Eq wt $= \frac{\text{at wt}}{\text{valency}}$ ∴ valency $= \frac{112}{55{\cdot}97} = 2.$

7. A current of 3·7 amperes is passed for 6 hrs between nickel electrodes in 0·5 litre of a 2M solution of $Ni(NO_3)_2$. What will be the molarity of the solution at the end of the electrolysis ?

I. I. T. (Group A) 1978.

1 litre nickel nitrate solution contains 2 gm mole $Ni(NO_3)_2$ before electrolysis.

0·5 ,, ,, ,, ,, ,, 2×0·5=1 gm mole ,, .

Now, 96500 coulombs of electricity is required to deposit 1 gm eq Ni.

or, " " " " " " " $\frac{1}{2}$ gm atom Ni.

$\therefore$ $3 \cdot 7 \times 6 \times 60 \times 60$ " " " " $\frac{1}{2} \times \frac{3 \cdot 7 \times 6 \times 60 \times 60}{96500}$

$= 0 \cdot 414$ gm atom Ni.

$$\left[1 \text{ gm equivalent wt} = \left(\frac{\text{at wt}}{\text{valency}} \right) \text{gm} = \left(\frac{\text{at wt}}{2} \right) \text{gm} = \tfrac{1}{2} \text{ gm atom} \right]$$

1 gm atom Ni≡1 gm mole Ni $(NO_3)_2$; 0·414 gm atom Ni≡ 0·414 gm mole Ni $(NO_3)_2$. So, 0·5 litre nickelnitrate soln contains (1−0·414)=0·586 gm mole Ni $(NO_3)_2$ after electrolysis.

$\therefore$ 1 litre nickel nitrate soln contains 0·586×2=1·172 gm mole Ni $(NO_3)_2$. Molarity of the solution at the end of the electrolysis=1·172.

8. An ammeter and a copper voltameter are connected in series through which a constant current flows. The ammeter shows 0·525 ampere if 0·6354 gm of copper is deposited in an hour, what is the percentage error of the ammeter ? (At wt of Cu=63·54).

West Bengal J. E. E. 1975.

$\frac{63 \cdot 54}{2}$ gm Cu is liberated by 96500 coulombs of electricity.

$\therefore$ 0·6354 " " " $\frac{96500 \times 2 \times 0 \cdot 6354}{63 \cdot 54} = 1930$ ".

Now, $1930 = C \times 60 \times 60$ or $C = \frac{1930}{3600} = 0 \cdot 536$ amp.

$$\%\text{error of the ammeter} = \frac{(0 \cdot 536 - 0 \cdot 525) \times 100}{0 \cdot 536} = 2 \cdot 052.$$

9. A current, passed for 6 minutes through a voltameter containing dilute H_2SO_4, liberated 40 cc of an electrolytic gas measured at 15°C and 748 mm pressure. What was the average value of the current ?

Calcutta U. B. Sc. *1971.*

We have, $\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$; $\frac{760 \times V_0}{273} = \frac{748 \times 40}{273 + 15}$

$\therefore$ $V_0 = 37 \cdot 31$

The liberated gas is a mixture of H_2 and O_2 and the volume of which at N.T.P is 37·31 cc. As $2H_2O \rightarrow 2H_2 + O_2$,

3 cc($H_2 + O_2$) mixture contain 2 cc H_2,

$\therefore$ 37·31 cc " " " $\frac{37{\cdot}31 \times 2}{3}$

$= 24{\cdot}87$ cc H_2 at N. T. P.

$\because$ 1 cc H_2 at N. T. P. weighs 0·00009 gm

$\therefore$ 24·87 cc " " weigh $0{\cdot}00009 \times 24{\cdot}87 = 0{\cdot}0022383$ gm.

We have now, $w = z.c.t$; $0{\cdot}0022383 = \frac{\text{eq. wt. of } H_2}{96{,}500} \times c \times 6 \times 60$

or, $0{\cdot}0022383 = \frac{1{\cdot}008}{96{,}500} \times c \times 6 \times 60$

$\therefore$ $c = \frac{0{\cdot}0022383 \times 96500}{1{\cdot}008 \times 6 \times 60} = 0{\cdot}595$ amp.

10. Ten grams of a fairly concentrated solution of cupric sulphate is electrolysed using 0·01 Faraday of electricity. Calculate (i) the weight of the resulting solution and (ii) the number of equivalents of acid or alkali in the solution.

I. I. T. (Gp. A) 1976.

(i) The weight of copper, deposited by 0·01 Faraday of electricity $= 0{\cdot}01 \times 31{\cdot}75 = 0{\cdot}3175$ gm.

$\because$ eq. wt. of $Cu = \frac{63{\cdot}5}{2} = 31{\cdot}75$. The weight of oxygen, liberated $= 0{\cdot}01 \times 8 = 0{\cdot}08$ gm. $\because$ eq. wt of $0_2 = 8$. $\therefore$ the weight of the resulting soln.

$= (10 - 0{\cdot}3175 - 0{\cdot}08)$ gm $= 9{\cdot}6025$ gm.

(ii) 0·01 Faraday of electricity produces 0·01 gm eq H_2SO_4 in soln.

11. Electric current is passed through two cells A and B in series. Cell A contains an aqueous solution of Ag_2SO_4 and platinum electrodes. Cell B contains aqueous solution of $CuSO_4$

and copper electrodes. The current is passed till 1·6 gm of oxygen is liberated at the anode of cell A. (i) Give equation for the reaction taking place at each electrode. (ii) Calculate the quantities of substances deposited at the cathodes of the two cells. *I. I. T. (Gp. A) 1975.*

(i) Equations: In cell A at the cathode, $Ag^+ + e \rightarrow Ag$; at the anode, $2H_2O \rightarrow 4H^+ + \uparrow O_2 + 4e$. In cell B at the cathode, $Cu^{2+} + 2e \rightarrow Cu$; at the anode, $2H_2O \rightarrow 4H^+ + \uparrow O_2 + 4e$. (ii) Gm eq of O_2 liberated $= \frac{1·6}{8} = 0·2$.

∴ gm eq Ag deposited $= 0·2$ and the weight of Ag deposited at the cathode $= 0·2 \times 108 = 21·6$ gms ; gm eq Cu deposited $= 0·2$ and the weight of Cu deposited at the cathode $= 0·2 \times 31·75 = 6·35$ gms.

Solubility and solubility product

12. The solubility of common salt at 40°C is 40 gms. 20 gms of an unsaturated solution of common salt at that temperature on evaporation gave 5 gms of salt. How much of common salt is to be added to 100 gms of this solution to make it saturated at that temperature ? *West Bengal H. S. (Comp.) 1975.*

140 gm saturated solution of common salt (100 gm solvent + 40 gm NaCl) at 40°C contain 40 gm common salt (NaCl).

∴ 100 gm saturated solution of common salt at 40°C contain $\frac{40 \times 100}{140} = 28·571$ gm common salt.

Again, 20 gms of an unsaturated solution of common salt at 40°C contain 5 gm salt. ∴ 100 gms of the unsaturated solution of common salt at 40°C contain $\frac{5 \times 100}{20} = 25$ gm salt.

∴ amount of common salt to be needed to make 100 gms of the unsaturated soln at 40°C saturated $= (28·571 - 25)$ gm $= 3·571$ gms.

13. Knowing the solubility of AgCl as 0·0015 gm per litre at 18°C, calculate the solubility product of this salt.

$\underset{S}{AgCl}\rightarrow\underset{S}{Ag^+}+\underset{S}{Cl^-}$, where S represents solubility of AgCl at 18°C.

Now, Ks = solubility product at 18°C = S^2

$$=\left(\frac{0{\cdot}0015}{\text{mol. wt. of AgCl}}\right)^2=\left(\frac{0{\cdot}0015}{108+35{\cdot}5}\right)^2=\left(\frac{0{\cdot}0015}{143{\cdot}5}\right)^2$$

$=1{\cdot}092\times10^{-10}$.

PH

14. The hydrogen ion concentration of solution is $31{\cdot}6\times10^{-5}$. What is its PH ? *Hyderabad I. Sc. 1973.*

$PH=-\log_{10}[H^+]=-\log_{10}31{\cdot}6\times10^{-5}$

$=-\log_{10}31{\cdot}6-\log_{10}10^{-5}$.

$=-1{\cdot}4997+5\log_{10}10=5-1{\cdot}4997=3{\cdot}5003$.

15. Calculate the concentration in normality of a NaOH solution of PH = 12·2. *Calcutta* U. B. Sc. 1977.

$PH=12{\cdot}2$ or, $12{\cdot}2=-\log_{10}[H^+]$ or, $[H^+]=10^{-12{\cdot}2}$

or, $[H^+]=10^{-12}.10^{-0{\cdot}2}=10^{-12}.10^{-0{\cdot}2}.10^{-1}.10^{1}$

$\because\ 10^{-1+1}=10^0=1$

or, $[H^+]=10^{-13}.10^{(1-0{\cdot}2)}=10^{0{\cdot}8}.10^{-13}$. Let $X=10^{0{\cdot}8}$

$\therefore\ \log_{10}X=0{\cdot}8$ by the definition of logarithm.

$X=$ anti log $\log_{10}X=$ anti log $0{\cdot}8=6{\cdot}310$.

So, $[H^+]=6{\cdot}310\times10^{-13}$. $\because\ [OH^-][H^+]=10^{-14}$

$$\therefore\ [OH^-]=\frac{10^{-14}}{6{\cdot}310\times10^{-13}}=\frac{1}{6{\cdot}310}10^{-1}.$$

or, $[OH^-]=0{\cdot}1584\times10^{-1}=1{\cdot}584\times10^{-2}$

$\therefore$ concentration $=1{\cdot}584\times10^{-2}$(N).

Problems for practice

Electrolysis

1. When 0·1 ampere current is passed through $CuSO_4$ soln for 100 minutes, 0·1978 gm copper is deposited. Calculate the

electrochemical equivalent of copper. *L. N. Mithila. U. 1973A.* Ans. 0·0003296.

2. A current of 0·5 ampere is sent through a solution of copper sulphate for 20 minutes using platinum electrodes. Calculate the number of copper atoms deposited. Cu=63·57. *West Bengal J. E. E. 1973.* Ans. $18·6713 \times 10^{20}$ atoms.

3. The density of copper is 8·94g/ml. Find out the number of coulombs needed to plate an area 10 cm × 10 cm to a thickness of 10^{-2}cm using $CuSO_4$ soln as electrolyte. *I. I. T. 1979.*

[Hints. Volume$=10\times10\times10^{-2}=1$ ml, amount of copper =8·94g, 96500 coulombs for $\frac{63·5}{2}$ gm Cu deposition.

Ans. 27171·968.]

4. 0·2964 gm of copper was deposited on passage of a current of 0·5 ampere for 30 minutes through a solution of copper sulphate. Calculate the atomic weight and electro chemical equivalent of copper. *Roorkee Adn. T. 1977 ; I. I. T. '72.* Ans. 63·56, $32·9\times10^{-5}$.

5. (a) For the electrolytic production of $NaClO_4$ from $NaClO_3$ as per the reaction : $ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e$ (i) How many faradays of electricity would be required to produce 1 gm mole of $NaClO_4$? (ii) What volume of H_2 at S. T. P. will be liberated at the cathode in the time that it takes to form 12·25 gms of $NaClO_4$? *I. I. T. (gp A) 1974 ; Calcutta.* U. B. Sc.*1974*. Ans. 2 ; 2·24 litres.

6. 0·1978 gm of copper was deposited by a current of 0·2 ampere in 50 minutes. What is the electro-chemical equivalent of copper ? *Patna.* U. *1974A.* Ans. 0·00003296.

7. A current of 1·5 ampere when passed for 30 minutes through the solution of a salt deposits 0·8898 gm of the metal on the cathode. The valency of the metal is 2. What is its atomic weight ? (1 Faraday=96,500 coulombs) *West Bengal H.S. 1975.* Ans. 63·592.

8. A current of 5 amperes is passed through copper sulphate

soln. How long current shall be passed to deposit 0·635 gm copper at the cathode ? [Cu=63·5, F=96, 500 coulombs]. *West Bengal H. S.* (*Tech.*) 1975. Ans. 386 sec.

9. Find out the amount of silver liberated when 0·075 ampere current is passed through a solution of $AgNO_3$ for 17 minutes. (Ag=108) *Ranchi.* U. *1975 S.* Ans. 0·0859 gm.

10. It is found that an electric current in 1 minute 40 seconds deposits 0·112 gm of silver and in twice the time 0·066 gm of copper. The equivalent weight of silver is 108. Find out the equivalent weight of copper. *Bhagalpur.* U. *1975* S. Ans. 31·83.

11. One hundred millilitres of 0·8 M copper sulphate is electrolysed for 30 minutes by passing a current of 5 amperes. Calculate the amount of copper sulphate in grams in the solution. *I. I. T. 1975.* Ans. 5·32 gms.

12. A solution of a salt of a metal of at wt 112 was electrolysed for 150 minutes with a current of 0·15 ampere. The weight of metal deposited was 0·783 gm. Find the valency of the metal in the salt. *West Bengal. J. E. E. 1976.* Ans. 2.

13. The weight of the cathode increases by 0·89 gm due to the deposition of a metal from a salt solution by passing a current of 1·5 amperes for 30 minutes. What is the equivalent weight of the metal ? (F=96,500 coulombs). *West Bengal H. S. C* (voc.). *1978.* Ans. 31·81.

14. Calculate the weight of pure refined copper that will be deposited on the cathode of an electrolytic refining cell using cupric sulphate as the electrolyte when 1500 ampere current is passed for 100 hrs. At. wt. of Cu=63·54. *West Bengal. J. E. E.* (*Tc*) *1978.* Ans. 177780·3 gms.

15. Calculate the amount of copper produced by the passage of 1·5 ampere electric current for an hr through copper sulphate solution. (Electrochemical equivalent of copper=0·00033) *Calcutta. U.* B. Sc. *1974.* Ans. 1·782 gm.

16. How much copper will deposit on the cathode of a voltameter if 2 Faradays' electricity is passed through a solution

of copper (II) sulphate ? 1 Faraday = 96,500 coulombs. Calculate the mass and number of atoms of silver deposited by 96500 C from a solution of silver nitrate and of copper deposited by 96500 C from a solution of copper sulphate. *I. S. C. E. 1978.* Ans. 63·5 ; 108 gms ; $6{\cdot}023 \times 10^{23}$; 31·75 and $3{\cdot}0115 \times 10^{23}$.

17. A current of 0·4825 ampere is passed through a metallic wire. What is the number of electrons passing per second through any point on the wire ? W. *B. H. S. C. 1979.*

[Hints. $e = \frac{96500}{6{\cdot}023 \times 10^{23}}$ amp/sec $\therefore$ no of electrons/sec = $3{\cdot}0115 \times 10^{18}$.]

18. The same quantity of electricity that liberated 4·316 gm of silver from silver nitrate solution was passed through a solution of gold salt. If the atomic weight of gold is 197·0 and its valency in the abovementioned salt is 3, calculate the weight of gold deposited at the cathode and the quantity of electricity passed. Given : Equivalent weight of silver = 107·9. *W.B.J.E.E. 1979.* Ans. 2·626 gms ; 3860 coulombs.

19. A current deposits 5gm of Cu in 1930 minutes from a solution of Cu^{2+} ions. What is the strength of the current in amperes ? How many gram of copper will the same current deposit during the same time from the solution of Cu^{+} ions ? *I.I.T. 1977.* Ans. 0·131 amp ; 10 gms.

20. Calculate the quantity of electricity that will be required for liberating 710 gms of chlorine gas by the electrolysis of concentrated solution of NaCl. What (i) weight of NaOH, (ii) volume of hydrogen measured at 27°C and 1 atm. pressure will be obtained during the process ? *I.I.T. 1977.* Ans. 20 Faradays ; 800 gms ; 246·1 litres.

21. An electric current is passed through the solutions of $CuSO_4$ and AgCN connected in series. If in a given time 0·35 gm of copper is deposited, what will be the weight of silver deposited in the same time ? Cu = 63·57 ; Ag = 107·8. *West Bengal J. E. E. 1970, 1971.* Ans. 1·187 gms.

22. A current of 965 amperes is passed through acidulated water for one minute and forty seconds. Find out the volume (at N.T.P.) of hydrogen evolved at the cathode and also the weight in gms of oxygen at the anode. *W. B. H. S. C. (Voc. 1980.).* Ans. 11·2 lits ; 8 gms.

23. An electric current is passed through solution of copper sulphate and silver nitrate connected in series. If in a given time 1·68 gm of silver is deposited, what will be the weight of copper deposited in the same time? ($Cu = 63·57$; $Ag = 107·88$). *Bihar. U. 1969* ; *Ranchi.* U. *1976 A.* Ans. 0·5 gm.

24. If electrochemical equivalent of Ag is 0·00118 then find out the electrochemical equivalent of oxygen. *L. N. M.* U. *1976A.* Ans. 0·0000829.

25. From the values of a Faraday and Avogadro's number, calculate the coulombic charge on an electron. *I. I. T.* (*gp A*). *1975.* Ans. $1·6 \times 10^{-19}$ coulombs.

26. Find the charge in coulombs of 1 gram ion of N^{3-}. *I. I. T.* 1980. Ans. $1·084 \times 10^{-4}$ coulombs.

Solubility and solubility product

27. 10·5 gms of a saturated solution of KCl at 40°C contains 3 gms of the salt. Calculate the solubility of the salt. *Hyderabad. I.Sc. 1977.* Ans. 40 gms.

28. The solubility product of AgCl is $2·8 \times 10^{-10}$ at 25°C. Calculate the solubility of the salt in pure water. *Delhi.* U. *1971.* Ans. $1·673 \times 10^{-5}$ gm mole/litre.

29. At a certain temperature the solubility of silver chromate is 3×10^{-2} gm per lit. Calculate its solubility product at that temperature ($Ag = 108$; $Cr = 52$). *Calcutta.* U. *B. Sc. 1978.* Ans. $2·951 \times 10^{-12}$.

[Hints. $\underset{S}{Ag_2CrO_4} \rightarrow \underset{2S}{2Ag^+} + \underset{S}{CrO_4''}$; $Ks = (2S)^2$. $S = 4S^3$.]

PH

30. What is the PH of a 0·2 M solution of KOH? *Hyderabad. I. Sc. 1975.* Ans. 13·3010.

31. Calculate the concentration in normality of an HCl solution of PH = 2·3. *Calcutta.* U. *B. Sc. 1975.* Ans. $5·012 \times 10^{-3}$(N).

32. What will be PH of the following liquids ? : (i) pure water (ii) 0·1NHCl (iii) 0·01NH_2SO_4. *Ranchi.* U. *1979.* Ans. (i) 7 (ii) 1 (iii) 2.

33. The PH of neutral water is 7 ; what is its P (OH) ? *Indian School certificate Examination, 1978.* Ans. 7.

34. (a) Two solns with PH values 2 and 6 are supplied. Which one is more acidic and how many times than the other ? (b) Calculate : (i) H^+ ion concn of a soln of PH=6·35. (ii) PH of a 0·1 N NaOH soln. *Calcutta.* U. *B. Sc.* (*New*) *1980.*

Ans. (a) PH=2 ; 10^4 times. (b) (i) $4·467\times10^{-7}$(N) ; (ii) 13.

Problems on ionic equilibrium

Examples : 1. Acetic acid is 4·5% dissociated in a N/10 solution at 20°C. Calculate the ionisation constant of the acid.

Acetic acid undergoes dissociation according to the following equation, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. Acetic acid is a weak electrolyte, law of mass action can be applicable to it according to Ostwald. By applying law of mass action to the above ionic equilibrium, we can write, $K=\frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$.

Let 1 gm mole acetic acid (CH_3COOH) be dissolved in 'V' litres of solution. α stands for degree of ionisation (dissociation).

Then, $[CH_3COO^-]=\frac{\alpha}{V}$; $[H^+]=\frac{\alpha}{V}$ and $[CH_3COOH]=\frac{1-\alpha}{V}$.

$$\text{So, } K=\frac{\frac{\alpha}{V}\cdot\frac{\alpha}{V}}{\frac{1-\alpha}{V}}=\frac{\alpha^2}{1-\alpha}\cdot\frac{1}{V}=\frac{\alpha^2}{1-\alpha}\,C \quad \because \frac{1}{V}=\text{concentration}=C.$$

Now, $K=\frac{(0·045)^2}{1-0·045}.0·1=2·10\times10^{-4}$. K is the ionisation constant (dissociation constant) at definite temperature.

2. At 30°C the degree of ionisation of formic acid in decinormal solution is 0·01133. What would be the degree of ionisation of this acid at the same temperature in centinormal solution ?

$$K=\frac{\alpha^2}{1-\alpha}.C \quad \because \quad \underset{1-\alpha}{HCOOH} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{COOH^-}.$$

$$K=\frac{(0·01133)^2}{(1-0·01133)}\times0·1\,; \quad K=\frac{\alpha_1{}^2}{1-\alpha_1}.0·01$$

or, $\frac{(0{\cdot}01133)^2 \times 0{\cdot}1}{(1-0{\cdot}01133)} = \frac{\alpha_1^2}{1-\alpha_1}.0{\cdot}01.$

$\therefore$ $\alpha_1 = 0{\cdot}036$. % ionisation at 30°C = 3·6.

3. The solubility product of lead iodide is 8×10^5. If the salt is 80% dissociated in saturated solution find the solubility of the salt. $\underset{S}{PbI_2} \rightleftharpoons \underset{S}{Pb^{++}} + \underset{2S}{2I^-}$

Let S be the solubility of lead iodide.

$Ks = S.(2S)^2 = 4S^3$ or, $8 \times 10^5 = 4S^3$.

$\therefore$ $S = 2{\cdot}714 \times 10^{-2}$ gm mole/litre.

As the salt is 80% dissociated, actual solubility

$= 2{\cdot}714 \times 10^{-2} \times \frac{100}{80} = 3{\cdot}392 \times 10^{-2}$ gm mole/litre

$= 3{\cdot}392 \times 10^{-2} \times 367 = 12{\cdot}45$ gms/litre

$\because$ molecular weight of lead iodide = 367.

Common ion effect

In presence of a common ion, the solubility of a solute decreases but the solubility product remains constant provided temperature is kept constant. This can be explained by taking an uni-univalent salt like AgCl. In solution $[Ag^+] = [Cl^-] = S$. Where, S stands for solubility of the salt. Ks = solubility product $= [Ag^+]\ [Cl^-] = S \times S = S^2$. Let us suppose that the solubility of silver chloride changes to S′ when *X* gm mole of sodium chloride is added to one litre solution. Sodium chloride will be totally ionised and will produce X gm equivalent of chloride ions. Under this circumstance, $[Ag^+] = S'$ and $[Cl^-] = (S' + X)$.

Hence, $Ks = S'(S' + X) = S^2$. $\therefore$ $S' \angle S$.

[1 gm mole NaCl = 1 gm equivalent NaCl]

4. Solubility product of leadchloride is $1{\cdot}8 \times 10^{-4}$. Find out the solubility of lead chloride in 0·1 (N)HCl.

Now, $[Pb^{+2}] = S$; $[Cl^-] = 0{\cdot}1 + 2S$ $\therefore$ $Ks = 1{\cdot}8 \times 10^{-4} = S(0{\cdot}1 + 2S)$

$\therefore$ $S = 0{\cdot}0517$ gm mole/litre. $\because$ $\underset{S}{PbCl_2} \rightleftharpoons \underset{S}{Pb^{++}} + \underset{2S}{2Cl^-}$

Problems for practice

1. The hydrogen ion concentration of a 0·1 (N) solution of a monobasic acid is $1{\cdot}3 \times 10^{-3}$N. Calculate the dissociation constant of the acid. *Calcutta. U. B. Sc. 1963*. Ans. $1{\cdot}712 \times 10^{-5}$.

2. The dissociation constant of an acid HA is $1{\cdot}8 \times 10^{-5}$. Calculate the hydrogen ion concentration of a 0·1 (N) solution of the acid HA. *Calcutta University. B. Sc. 1967 ; '69.* Ans. $1{\cdot}371 \times 10^{-3}$N.

3. The solubility of barium sulphate at 25°C is 0·00233 gm per litre. Calculate the solubility product of the salt, assuming that it is totally ionised at the concentration mentioned. What will be the solubility of barium sulphate at 25°C in an ammonium sulphate solution containing 13·2 gms of ammonium sulphate per litre, assuming complete dissociation of ammonium sulphate. Ans. 10^{-10} ; $2{\cdot}33 \times 10^{-7}$ gm/litre.

4. The solubility of Ag_2CO_3 in water is $1{\cdot}16 \times 10^{-4}$ mole/litre. Calculate its solubility in 0·01 (N) $AgNO_3$ solution, after making necessary approximation. *Calcutta.* U. *B. Sc.* 1973. Ans. $6{\cdot}24 \times 10^{-8}$ mole/litre [Hints. (neglect S'^3 and S'^2 terms)]

5. At a certain temperature the solubility of silver chromate is 3×10^{-2} gm/litre. Calculate its solubility product at that temperature (Ag = 108, Cr = 52). *Calcutta.* U. *B. Sc. 1978.* Ans. $2{\cdot}451 \times 10^{-12}$.

6. The solubility product of AgCl in water $2{\cdot}8 \times 10^{-10}$ at 25°C. Calculate the solubility of AgCl at this temperature. *Delhi. 1971.* Ans. $1{\cdot}6 \times 10^{-5}$ gm mole/lit.

7. Calculate the degree of dissociation α of acetic acid (diss. const = $1{\cdot}75 \times 10^{-5}$) in (i) a 0·02 molar solution of acetic acid, and (ii) 0·02 molar solution of acetic acid containing 0·005 molar sodium acetate. (In both cases, consider $\alpha << 1$). *Calcutta University B. Sc. 1977.* Ans. 2·958% ; 0·35%.

CHAPTER 12

Problems on dilute solution, distribution law and Henry's law :

Dilute solution :

A homogeneous mixture of two or more substances is called *solution*. The component present in the greatest quantity is known as a *solvent* while the other in smaller quantity is known as a *solute*. In *dilute solution*, solute is present in a very small quantity as compared to solvent.

Colligative properties of dilute solution :

The certain physical properties of a dilute solution which depend on the number of moles of the solute and not on their nature are called colligative properties of dilute solution. They are lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure.

Lowering of vapour pressure :

The vapour pressure of a pure solvent (liquid) gets lowered down when a non volatile non electrolyte solute (solid) is dissolved in it. Let the vapour pressure of the pure solvent be p_0 and the vapour pressure of the solution be p, the lowering of vapour pressure will then be $p_0 - p$. $\frac{p_0 - p}{p_0}$ is known as relative lowering of vapour pressure. It is defined as the ratio of the lowering of vapour pressure to the vapour pressure of the pure solvent.

Raoult's law : The law states that the relative lowering of vapour pressure is equal to the mole fraction of the solute. The law can mathematically be expressed as :

$\frac{p_0 - p}{p_0} = \frac{n_1}{n_1 + n_2}$ Where, n_1 and n_2 represent number of moles of solute and solvent respectively.

or, $\frac{p_0 - p}{p_0} = \frac{W_1/M_1}{W_1/M_1 + W_2/M_2}$ Where, $n_1 = W_1/M_1$; $n_2 = W_2/M_2$. W_1 and W_2 represent weights in gms of the solute and solvent respectively. M_1 and M_2 stand for molecular weights of the solute and solvent respectively.

Abnormality in vapour pressure measurement :

Abnormality in vapour pressure measurement is seen by electrolytes as solute (viz. NaCl, Ca $(NO_3)_2$ etc), present in the solution. Electrolytes yield ions partially in the solution which fluctuate the vapour pressure. Thus, abnormality is noted. The above Raoult's law expressions are then modified according to the type of electrolyte dissolved.

For uni-uni valent electrolyte (viz. NaCl),

$$\frac{p_0-p}{p_0}=\frac{(1+\alpha)n_1}{(1+\alpha)n_1+n_2}\,;\quad \underset{1-\alpha}{NaCl}\rightleftharpoons\underset{\alpha}{Na^+}+\underset{\alpha}{Cl^-}$$

or, $$\frac{p_0-p}{p_0}=\frac{(1+\alpha)\frac{W_1}{M_1}}{(1+\alpha)\frac{W_1}{M_1}+\frac{W_2}{M_2}}.$$

Total number of particles after dissociation (ionisation) $=1-\alpha+\alpha+\alpha=1+\alpha$.

Where, α = degree of ionisation.

For bi-uni valent electrolyte [viz. Ca $(NO_3)_2$],

$$\frac{p_0-p}{p_0}=\frac{(1+2\alpha)n_1}{(1+2\alpha)n_1+n_2}\,;\quad \underset{1-\alpha}{Ca(NO_3)_2}\rightleftharpoons\underset{\alpha}{Ca^{++}}+\underset{2\alpha}{2NO_3^-}$$

or, $$\frac{p_0-p}{p_0}=\frac{(1+2\alpha)\frac{W_1}{M_1}}{(1+2\alpha)\frac{W_1}{M_1}+\frac{W_2}{M_2}}.$$

Total number of particles after ionisation $=1-\alpha+\alpha+2\alpha=1+2\alpha$.

For bi-bi valent electrolyte (viz. $CaSO_4$),

$$\frac{p_0-p}{p_0}=\frac{(1+\alpha)n_1}{(1+\alpha)n_1+n_2}\,;\quad \underset{1-\alpha}{CaSO_4}\rightleftharpoons\underset{\alpha}{Ca^{++}}+\underset{\alpha}{SO_4^{--}}$$

or, $$\frac{p_0-p}{p_0}=\frac{(1+\alpha)\frac{W_1}{M_1}}{(1+\alpha)\frac{W_1}{M_1}+\frac{W_2}{M_2}}.$$

Total number of particles after ionisation $=1-\alpha+\alpha+\alpha=1+\alpha$.

Solved problems :

1. A solution contains 5 gms of urea (molecular weight=60) per 100 gms of water. What will be the vapour pressure of this solution at 25°C ? The vapour pressure of pure water at this temperature is 23·76 mm. *Calcutta.* U. *B. Sc. 1978.*

$$\frac{p_0-p}{p_0}=\frac{W_1/M_1}{W_1/M_1+W_2/M_2} \text{ or, } \frac{23{\cdot}76-p}{23{\cdot}76}=\frac{5/60}{5/60+\frac{100}{18}}$$

$$\therefore \; p=23{\cdot}084 \text{ mm.}$$

2. Given the density of water to be 1 gm|cc which of the following two solutions will have lower vapour pressure ?

(i) **1** molal aqueous solution of cane sugar. (ii) A cane sugar solution in which the mole fraction of cane sugar is **0·1.** *Calcutta.* U. *B.Sc. 1977.*

(i) $\frac{p_0-p}{p_0}=\frac{n_1}{n_1+n_2}$ or, $\frac{p_0-p}{p_0}=\frac{1}{1+\frac{1000}{18}}=\frac{18}{1018}$

or, $1-\frac{p}{p_0}=\frac{18}{1018}$ or, $1-\frac{18}{1018}=\frac{p}{p_0}$ or, $\frac{p}{p_0}=\frac{1000}{1018}$

or, $p=\frac{1000}{1018}p_0$ or, $p=0{\cdot}982\,p_0$ $\because$ 1 molal soln=**1** gm mole solute dissolved in 1000 gm solvent.

(ii) $\frac{p_0-p}{p_0}=0{\cdot}1$ or, $1-\frac{p}{p_0}=0{\cdot}1$ or, $1-0{\cdot}1=\frac{p}{p_0}$ or, $p=0{\cdot}9\,p_0$. Since the vapour pressure of pure water (p_0) becomes constant at definite temperature, the vapour pressure of 1 molal aqueous solution of canesugar is greater than that of the cane sugar solution in which the mole fraction of cane sugar is 0·1.

3. The vapour pressure of a solution containing 6·69 gms of $Ca(NO_3)_2$ in 100 gms of water is 746·9 mm of Hg at 100°C. What is the degree of dissociation of the salt ? [Molecular weight of $Ca(NO_3)_2$=164] *Calcutta.* U. *B. Sc. 1974.*

$$\frac{p_0-p}{p_0}=\frac{(1+2\alpha)\frac{W_1}{M_1}}{(1+2\alpha)\frac{W_1}{M_1}+\frac{W_2}{M_2}}\;; \quad \underset{1-\alpha}{Ca(NO_3)_2} \rightleftharpoons \underset{\alpha}{Ca^{++}} + \underset{2\alpha}{2NO_3^-}$$

$$\text{or,}\quad \frac{760-746{\cdot}9}{760}=\frac{(1+2\alpha)\frac{6{\cdot}69}{164}}{(1+2\alpha)\frac{6{\cdot}69}{164}+\frac{100}{18}}.$$

Total number of particles $=1+2\alpha$. α stands for degree of dissociation.

$\alpha=0{\cdot}699$ $\therefore$ %dissociation $=69{\cdot}9$.

4. Dry air was passed through a solution containing 50 gms of a solute in 100 gms of water and then through water. The loss in weight of water was 0·05 gm. The wet air was then passed through concentrated sulphuric acid whose weight was increased by 2 gms. What is the molecular weight of the dissolved substance ? *Lucknow*. U. *1969*.

$\frac{p_0-p}{p_0}=\frac{W_1/M_1}{W_1/M_1+W_2/M_2}$ or, $\frac{p_0-p}{p_0}=\frac{50/M_1}{50/M_1+\frac{100}{18}}$. Now, loss in weight of water $=0{\cdot}05=k(p_0-p)$ and gain in weight of H_2SO_4 $=2=kp_0$. Where, $k=$ proportionality constant.

$$\text{or,}\quad \frac{0{\cdot}05}{2}=\frac{50/M_1}{50/M_1+\frac{100}{18}}\qquad \therefore\ M_1=351.$$

Elevation of boiling point :

Boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to 760 mm of Hg i.e., normal atmospheric pressure. Elevation of boiling point is seen when a non-volatile and non-electrolyte solute is added to a solvent (liquid). There are two laws on the elevation of boiling point due to Raoult. The laws stated as follows :

Law 1 : The elevation of boiling point of a solvent by a dissolved solute is directly proportional to the molality of the solution.

Law 2. Equimolecular amounts of different solutes dissolved in the same amount of the same solvent elevate the boiling point to the same extent.

From Law 1, $\Delta T_b \propto Cm$. $\left\{\begin{array}{l}\text{Where, } Cm = \text{molality of the solution,}\\ \Delta T_b = \text{elevation of boiling point.}\end{array}\right.$
If 'a' gms of a solute of

molecular weight M be dissolved in b gms of a solvent, then $Cm=\frac{a\times 1000}{b\times M}$. $\therefore\ \Delta T_b \propto \frac{a\times 1000}{b\times M}$ or, $\Delta T_b=K_b\,\frac{a\times 1000}{b\times M}$.

Where, K_b is a constant for the solvent, known as the **ebullioscopic constant or molal elevation of boiling point constant.** When $a=M$ and $b=1000$ i.e.; $Cm=1$ molal, we can write, $\Delta T_b=K_b$. Hence the ebullioscopic constant or the molal boiling point elevation constant of a solvent may be defined as the elevation of boiling point of the solvent when 1 mole of a non-volatile and non-electrolyte solute is dissolved per 1000 gms of the solvent.

From Van't Hoff's theoretical formula, we have,

$K_b=\frac{0{\cdot}002T_0^2}{lv}$. Where, T_0 = boiling point of pure solvent in °A, lv = latent heat of vaporisation of pure solvent in cals per gm.

For water, $T_0=373^\circ$A and $lv=540$ cals/gm.

$$\therefore\ K_b=\frac{0{\cdot}002\times(373)^2}{540}=0{\cdot}5152.$$

Abnormal elevation of boiling point :

Abnormality in boiling point measurement is noted due to electrolyte as solute present in the solution. The Raoult's law expression is then modified with respect to the type of electrolyte dissolved.

For uni-uni valent electrolyte (viz. KCl),

$$\Delta T_b=K_b\frac{(1+\alpha)a\times 1000}{b\times M};\quad \underset{1-\alpha}{KCl}\rightleftharpoons\underset{\alpha}{K^+}+\underset{\alpha}{Cl^-}.$$

Total number of particles after dissociation $=1-\alpha+\alpha+\alpha=1+\alpha$. Where, α = degree of dissociation (ionisation).

For bi-uni valent electrolyte [viz. $Ba(NO_3)_2$],

$$\Delta T_b=K_b\,\frac{(1+2\alpha)a\times 1000}{b\times M};\quad \underset{1-\alpha}{Ba(NO_3)_2}\rightleftharpoons\underset{\alpha}{Ba^{++}}+\underset{2\alpha}{2NO_3^-}.$$

Total number of particles after ionisation $=1-\alpha+\alpha+2\alpha=1+2\alpha$. Where, α = degree of ionisation.

For bi-bi valent electrolyte [viz. $FeSO_4$],

$\Delta T_b = K_b \frac{(1+\alpha)a \times 1000}{b \times M}$. For $\underset{1-\alpha}{FeSO_4} \rightleftharpoons \underset{\alpha}{Fe^{++}} + \underset{\alpha}{SO_4^{--}}$; total number of particles after ionisation $= 1-\alpha+\alpha+\alpha = 1+\alpha$.

Where, α = degree of ionisation ; i = Van't Hoff's factor

$$= \frac{\text{Observed elevation of boiling point}}{\text{Theoretical elevation of boiling point}} = \frac{\Delta T_b}{\Delta T_b{}^0}.$$

$i = 1+\alpha$ for uni-uni and bi-bi valent electrolyte.

$i = 1+2\alpha$ for uni-bi or bi-uni valent electrolyte.

Solved problems :

1. A 5% (wt/wt) aqueous solution of a substance shows a boiling point elevation of 0·85°C ; calculate its molecular weight. (Given : molal boiling point elevation constant of water = 0·516°C). *Calcutta*. U. *B.Sc. 1977*.

$$\Delta T_b = K_b \frac{a \times 1000}{b \times M} \quad \text{or,} \quad 0{\cdot}85 = \frac{0{\cdot}516 \times 5 \times 1000}{100 \times M} \quad \therefore M = 31{\cdot}96.$$

2. The normal boiling point of $CHCl_3$ is 61·20°C and its heat of vaporisation is 59 cals/gm. In 50 gms of $CHCl_3$ is dissolved 0·5 gm of an organic substance and the boiling point of the solution is 61·42°C. Calculate the molecular weight of the solute. *Calcutta*. U. *1970*.

$$K_b = \frac{0{\cdot}002T_0{}^2}{l_v} = \frac{0{\cdot}002(273+61{\cdot}42)^2}{59} = 3{\cdot}786.$$

Now, $\Delta T_b = K_b \frac{a \times 1000}{M \times b}$ or, $61{\cdot}42 - 61{\cdot}20 = \frac{3{\cdot}786 \times 0{\cdot}5 \times 1000}{M \times 50}$

$\therefore M = 172{\cdot}09.$

3. 1·23 gm $Ca(NO_3)_2$ is dissolved in 10 gm water. Boiling point of the solution is 100·975°C. Calculate the degree of ionisation of $Ca(NO_3)_2$. Molal elevation per 1000 gm water = 0·52°C. *Magadh*. U. *1975* S.

$$\Delta T_b = K_b \frac{(1+2\alpha)a \times 1000}{b \times M}$$

$$\text{or,} \quad (100{\cdot}975 - 100) = \frac{0{\cdot}52(1+2\alpha) \times 1{\cdot}23 \times 1000}{10 \times 164}$$

$\therefore \alpha = 0{\cdot}75$ or, % ionisation = 75 [Mol wt of $Ca(NO_3)_2$ = 164].

4. A solution of 3g of a substance in 100g of water had a boiling point of 100·26°C. Calculate the molecular weight of the substance if the molal elevation constant of water is 0·52.

I. S. C. E. 1979.

$$T_b = K_b \times \frac{a \times 1000}{b \times M} \quad \text{or,} \quad 0{\cdot}26 = \frac{0{\cdot}52 \times 3 \times 1000}{100 \times M}$$

$$\therefore \quad M = \frac{0{\cdot}52 \times 30}{0{\cdot}26} = \frac{5{\cdot}2 \times 3}{0{\cdot}26} = \frac{15{\cdot}6}{0{\cdot}26} = 60.$$

5. What is the boiling point of a solution containing 10 gms of urea (CON_2H_4) in 100 gms of water [K_{100} for water $= 5{\cdot}2$]

Magadh. U. *1969*A.

K_{1000} for water $= \frac{5{\cdot}2}{10} = 0{\cdot}52.$

$$\text{Now,} \quad \Delta T_b = \frac{0{\cdot}52 \times 10 \times 1000}{100 \times 60}$$

Or, $\Delta T_b = 0{\cdot}866$°C $\because$ boiling point of pure water $= 100$°C

$\therefore$ boiling point of the solution $= 100 + 0{\cdot}866 = 100{\cdot}866$°C.

6. 1gm sugar is dissolved in 105 gm water. Boiling point of the solution at 760 mm pressure is 100·060°C. How much water is to be added to the solution so that the boiling point of the solution decreases to 100·045°C. *Magadh.* U. *1976 A.*

$$\Delta T_b = K_b \ \frac{a \times 1000}{b \times M} \quad \text{or,} \ 0{\cdot}060 = K_b \ \frac{1 \times 1000}{105 \times 342}$$

$\because$ mol. wt. of sugar $= 342$.

$\therefore$ $K_b = 2{\cdot}1546$. Again, $0{\cdot}045 = \frac{2{\cdot}1546 \times 1 \times 1000}{b \times 342}$.

$\therefore$ $b = 139{\cdot}25$ gms $=$ amount of solvent.

Amount of water added to the soln $= (139{\cdot}25 - 105)$ gms $= 34{\cdot}25$ gms.

Depression of freezing point :

Laws on depression of freezing point :

Law 1 : The depression of freezing point of a solvent by added non-volatile and non-electrolyte solute is directly proportional to the molality of the solution.

Law 2. Equimolecular quantities of different solutes dissolved in the same quantity of the same solvent decrease the freezing point to the same extent.

In the similar manner as in the case of elevation of boiling point, the expression, $\triangle T_f = K_f \frac{a \times 1000}{b \times M}$, can be deduced.

Where, $\triangle T_f$ = depression in freezing point ; a = amount of solute in gms ; b = amount of solvent in gms ; M = molecular weight of the solute and K_f = a constant, known as the cryoscopic constant or the molal depression of freezing point constant. Similar to elevation of boiling point, the cryoscopic constant or the molal freezing point depression constant of a solvent may be defined as the depression of the freezing point of the solvent when 1 mole of a non-volatile and non-electrolyte is dissolved per 1000 gms of the solvent.

From Van't Hoff's theoretical formula,

$K_f = \frac{0{\cdot}002 T_0^2}{l_f}$, where, T_0 = freezing point of pure solvent in °A, l_f = latent heat of fusion or melting of pure solid solvent in cals per gm.

For water, $T_0 = 273°A$ and $l_f = 80$ cals/gm.

$$\therefore \quad K_f = \frac{0{\cdot}002 \times (273)^2}{80} = 1{\cdot}863.$$

Abnormal depression of freezing point :

Abnormality in freezing point determination is observed because of electrolyte as solute being present in the solution. The Raoult's law expression is corrected then with respect to the type of electrolyte dissolved in the solution.

For uni-uni valent electrolyte, bi-uni valent electrolyte the corrected expressions are,

$\triangle T_f = K_f \frac{(1+\alpha)a \times 1000}{b \times M}$ and $\triangle T_f = K_f \frac{(1+2\alpha)a \times 1000}{b \times M}$ respectively.

$\triangle T_f = \frac{K_f(1+\alpha)a \times 1000}{b \times M}$ for bi-bi valent electrolyte.

i = Van't Hoff's factor = $\dfrac{\text{observed depression of freezing point}}{\text{theoretical depression of freezing point}}$

$= \dfrac{\Delta T_f}{\Delta T^0_f} = 1+\alpha$ for uni-uni and bi-bi valent electrolyte.

$i = 1+2\alpha$ for uni-bi or bi-uni valent electrolyte.

Solved problems :

1. A solution of 0·873 gm of a substance in 50 gms of benzene showed a freezing point depression of 0·75°C. Calculate the molecular weight of the substance if the molal freezing point depression constant of benzene be 5·12. *Calcutta.* U. *B.Sc. 1975.*

$$\Delta T_f = K_f . \frac{a \times 1000}{b \times M} \text{ or, } 0{\cdot}75 = \frac{5{\cdot}12 \times 0{\cdot}873 \times 1000}{50 \times M} \therefore M = 119{\cdot}2.$$

2. The heat of fusion of acetic acid is 44·7 cals/gm at the melting point 16·6°C. Calculate the molal freezing point deression constant (K_f) for acetic acid. *Calcutta.* U. *B. Sc. 1972.*

$$K_f = \frac{0{\cdot}002\, T_0^2}{l_f} = \frac{0{\cdot}002(273+16{\cdot}6)^2}{44{\cdot}7} = 3{\cdot}75$$

[∵ melting pt = freezing pt]

3. 1·26 gm NaCl is dissolved in 50 gm water. Freezing point of the solution is 1·53°C. Calculate the degree of ionisation of NaCl. [K_f per 1000 gm water = 1·86] *Magadh.* U. *1974S.*

$$\Delta T_f = K_f \frac{(1+\alpha)a \times 1000}{b \times M} \text{ or, } 1{\cdot}53 = \frac{1{\cdot}86(1+\alpha)1{\cdot}26 \times 1000}{50 \times (23+35{\cdot}5)}$$

$\therefore$ $\alpha = 0{\cdot}9098$. %dissociation = 90·98.

4. The freezing point of water was lowered by 0·19°C by dissolving 0·152 gm of the substance in 25 gms of water. Calculate the molecular weight of the substance. Molecular depression constant of water (100gm) = 18·5. *Indian School certificate Examination, 1978.*

$$K_{f(1000)} = \frac{K_{f(100)}}{10} = \frac{18{\cdot}5}{10} = 1{\cdot}85. \text{ Now, } \Delta T_f = K_f . \frac{a \times 1000}{b \times M}$$

$$\text{or, } 0{\cdot}19 = \frac{1{\cdot}85 \times 0{\cdot}152 \times 1000}{25 \times M} \quad \therefore M = 59{\cdot}2.$$

5. 1·355 gm of a substance dissolved in 55 gms of acetic acid produced a depression of 0·618°C in the freezing point. Calculate the molecular weight of the dissolved substance. The molecular depression of freezing point of acetic acid is 38·5°C in 100 gms of acetic acid. *Bihar.* U. *1967 A*, *'69A* ; *Magadh.* U. *'73S*, *'74S* ; *Patna.* U. *'75A*.

$$K_f(1000)=\frac{K_f(100)}{10}=\frac{38{\cdot}5}{10}=3{\cdot}85. \text{ Now, } \Delta T_f=K_f.\ \frac{a\times 1000}{b\times M}$$

$$\text{or, }\ 0{\cdot}618=\frac{3{\cdot}85\times 1{\cdot}355\times 1000}{55\times M}\quad \therefore\ M=153{\cdot}5.$$

6. When 0·32 gm of naphthalene ($C_{10}H_8$) is dissolved in 40 gms of benzene, the freezing point of benzene is lowered by 0·312°C. When 0·4 gm of another substance is dissolved in 55 gms of the same solvent, the observed depression of freezing point is 0·252°C. Find the molecular weight of the second substance. *Patna.* U. *1974 A*, *1975A*.

$$\Delta T_f=K_f\frac{a\times 1000}{b\times M}\quad \text{or, }\ 0{\cdot}312=K_f\frac{0{\cdot}32\times 1000}{40\times 128}\quad \therefore\ K_f=4{\cdot}992.$$

$$\text{Again, }\ 0{\cdot}252=\frac{4{\cdot}992\times 0{\cdot}4\times 1000}{55\times M}\quad \therefore\ M=144{\cdot}07.$$

Osmosis and osmotic pressure :

Phenomenon of the spontaneous flow of solvent molecules from the solution of lower concentration to higher concentration when they are separated by a semi-permeable membrane, is called *osmosis*.

Semi permeable membrane : A membrane which allows the solvent molecules to pass through it but not to solute molecules is known as semi permeable membrane. e.g., cellophane paper, calcium silicate, egg shell, copper ferrocyanide [$Cu_2Fe(CN)_6$], animal bladder etc.

Osmotic pressure : It is the mechanical pressure that must be applied on a solution to prevent osmosis of the solvent into the solution.

Laws of osmotic pressure :

1. At constant temperature the osmotic pressure of a solution is directly proportional to its concentration.

2. At the definite concentration of a solution, the osmotic pressure of the dilute solution is directly proportional to its temperature.

3. Under the same conditions of temperature and osmotic pressure equal volumes of all solutions contain an equal number of moles of solute.

From 1st and 2nd Law of osmotic pressure, we can write $P = CRT$. Where, P = osmotic pressure, C = concentration of solution, R = a constant having magnitude equal to molar gas constant and T = absolute temperature of the solution. This equation is known as Van't Hoff's equation for osmotic pressure.

or, $P = \frac{n}{V}RT$. Where, $C = \frac{n}{V}$, n = number of gm moles of solute and V = volume of the solution in litres. When P is expressed in atmospheres, $R = 0{\cdot}0821$ lit. atm/deg/mole.

or, $PV = nRT = \frac{W}{M}RT \quad \because \quad n = \frac{W}{M}$. Where, W = weight of solute in gms and M = molecular weight of the solute.

Abnormal osmotic pressure :

Abnormality in osmotic pressure determination is observed because of electrolyte as solute being present in the solution. The above expressions are then corrected according to the type of electrolyte dissolved in the solution.

For uni-uni valent electrolyte :

$$P = (1+\alpha)CRT \; ; \; P = (1+\alpha)\frac{n}{V}RT \; ; \; PV = (1+\alpha)\frac{W}{M}RT.$$

For uni-bi valent electrolyte :

$$P = (1+2\alpha)\,CRT \; ; \; P = (1+2\alpha)\frac{n}{V}RT \; ; \; PV = (1+2\alpha)\frac{W}{M}RT.$$

For bi-bi valent electrolyte :

$P=(1+\alpha)\,CRT$; $P=(1+\alpha)\frac{n}{V}RT$; $PV=(1+\alpha)\frac{W}{M}RT$.

Where, α stands for degree of ionisation.

$i=$ Van't Hoff's factor $=\frac{\text{observed osmotic pressure}}{\text{theoretical osmotic pressure}}$.

$i=1+\alpha$ for uni-uni valent electrolyte.

$i=1+\alpha$ „ bi-bi „ „ .

$i=1+2\alpha$ „ uni-bi „ „ .

Isotonic solutions :

The solutions having same osmotic pressure are called isotonic solutions.

Solved problems :

1. 2·25 gms of a non-volatile solute when dissolved in 500 ml of water exert an osmotic pressure of 0·6 atmosphere at 25°C. Calculate the molecular weight of the solute. *Bombay.* U. *I. Sc. 1976.*

$PV=\frac{W}{M}RT$ or, $0{\cdot}6\times\frac{500}{1000}=\frac{2{\cdot}25}{M}\,0{\cdot}0821\times(273+25)$

$\therefore\ M=183{\cdot}27.$

2. Calculate the osmotic pressure of a 0·825(M) sucrose solution at 20°C. *Calcutta. U. B. Sc. 1978.*

$P=CRT$ or, $P=0{\cdot}825\times0{\cdot}0821\times(273+20)=19{\cdot}84$ atms.

3. A 1% solution of KCl is dissociated to the extent of 80%. What would be its osmotic pressure at 27°C ? *Gorakpur.* U. *1969.*

$PV=(1+\alpha)\frac{W}{M}RT$ or, $P.\,\frac{100}{1000}=(1+\alpha)\frac{1}{(39+35{\cdot}5)}0{\cdot}0821\times T$

or, $P.\,0{\cdot}1=(1+0{\cdot}8)\,\frac{1}{74{\cdot}5}\times0{\cdot}0821\times(273+27)$

or, $P=\frac{1{\cdot}8\times0{\cdot}0821\times300}{0{\cdot}1\times74{\cdot}5}=5{\cdot}942$ atms.

4. A solution containing 11gm per litre of a non electrolyte having a molecular weight of 60 was found to be isotonic with a

decinormal solution of sodium chloride. What is the apparent degree of ionisation of sodium chloride ? *Calcutta.* U. *B.Sc. 1969.*

$P.\,1=\frac{11}{60}\,RT\cdots\text{(i)}\ ;\quad P.\,1=(1+\alpha)\frac{1}{10}\,RT\ldots\text{(ii)}$

$\because$ 1gm mole NaCl = 1 gm equivalent NaCl. From equation (i) and (ii), we can write, $\frac{11}{60}\,RT=(1+\alpha)0{\cdot}1RT.$

$\therefore$ $\alpha=0{\cdot}83.$% dissociation (ionisation) = 83.

5. At 27°C an aqueous solution of a carbohydrate containing 18gms per 100ml of the solution is found to be isotonic with another aqueous solution 100ml of which contain 2·923 gms of sodium chloride. What is the molecular weight of the carbohydrate ? [Na = 23 ; Cl = 35·45] *Calcutta.* U. *B. Sc. 1978.*

$$P.\frac{100}{1000}=\frac{18}{M}\,0{\cdot}0821(273+27)\ \cdots\ \text{(i)}$$

$$P.\frac{100}{1000}=(1+\alpha)\frac{2{\cdot}923}{58{\cdot}45}\times0{\cdot}0821(273+27)$$

$$\text{or,}\quad P.\frac{100}{1000}=(1+1)\frac{2{\cdot}923}{58{\cdot}45}\times0{\cdot}0821(273+27)\cdots\text{(ii)}$$

$\because$ $\alpha=1$ (assuming cent percent ionisation of NaCl). From equation (i) and (ii), $\frac{18}{M}=\frac{2\times2{\cdot}923}{58{\cdot}45}$ $\therefore$ $M=179{\cdot}969.$

6. The osmotic pressure of a solution of urea at 10°C is 500 mm of mercury. If the solution is diluted ten times its original volume, what will be the osmotic pressure of the diluted solution at 15°C ? *Patna.* U. 1969 *A.*

$$PV=nRT\ \text{or,}\ \frac{500}{760}\times V=n.0{\cdot}0821(273+10)\cdots\text{(i)}$$

Now, volume of the solution = 10V litres.

$P.\ 10\,V=n.0{\cdot}0821\times(273+15)\ldots\text{(ii)}$

From equation (i) and (ii) we can write,

$$\frac{500\times V}{760\times283}=\frac{P.10V}{288}\ \therefore\ P=\frac{500\times1\times288}{760\times283\times10}=\frac{5\times288}{76\times283}$$

$$=0{\cdot}066\ \text{atm.}$$

7. Calculate the osmotic pressure of a solution obtained by mixing (a) 100 cc of 1·5% solution of urea (M=60) and (b) 100cc

of 3·42% solution of cane sugar (M=342) at 20°C. *Magadh. U. 1963, 1975A.*

100 cc urea solution contain $\frac{1·5}{60}=0·025$ gm mole urea.

100 cc cane sugar solution contain $\frac{3·42}{342}=0·01$ gm mole cane sugar.

∴ 200cc mixed solution contain (0·025+0·01) gm mole= 0·035 gm mole urea and canesugar.

As the osmotic pressure depends on number of moles of solute and not on their nature, we can write.

$$P.\frac{200}{1000}=0·035\times0·0821\times(273+20)$$

$$\text{or,}\quad P\times0·2=0·035\times0·0821\times293$$

$$\text{or,}\quad P=\frac{0·035\times0·0821\times293}{0·2}=4·209 \text{ atms.}$$

8. A solution of cane sugar is in equilibrium with ice at −2°C. Calculate the osmotic pressure of the solution at this temperature, given that K_b for 100 gms of water is 18·6°C. *Magadh. U. 1973S.*

18·6°C depression in freezing point is noted when 1 gm mole cane sugar dissolved in 100gm water.

∴ 2°C depression in freezing point is noted when $\frac{2}{18·6}$ gm mole$=\frac{1}{9·3}$ gm mole cane sugar dissolved in 100gm water. For dilute solution, volume of solvent≈volume of solution.

∴ 100cc solution contain $\frac{1}{9·3}$ gm mole canesugar.

∵ density of water=1.

$$\text{Now, } PV=nRT \quad \text{or,}\quad P\frac{100}{1000}=\frac{1}{9·3}\times0·0821\times(273-2)$$

$$\text{or,}\quad P\times0·1=\frac{0·0821\times271}{9·3} \quad \text{or,}\quad P=\frac{0·0821\times271}{9·3\times0·1}=23·923 \text{ atms.}$$

Distribution Law :

When a solute is dissolved in two liquids immiscible with each other, the solute gets distributed in two liquids in such a way that a constant ratio exists between the concentrations of the solute at a given temperature. This constant ratio is called distribution ratio or distribution coefficient or partition coefficient. Mathematically, K = distribution ratio

$$=\frac{\text{concentration of solute in liquid A}}{\text{concentration of solute in liquid B}} \text{ at a given temperature.}$$

Solved problem :

At a given temperature the solubility of iodine in water is 0·35 gm/lit. What will be its solubility in CCl_4 ? (Distribution ratio of iodine in CCl_4 and water is 88). *Calcutta.* U. *B. Sc. 1978.*

$$\text{Distribution ratio of iodine}=\frac{\text{solubility of iodine in } CCl_4}{\text{solubility of iodine in water}}$$

$$\text{or,}\quad 88=\frac{\text{solubility of iodine in } CCl_4}{0{\cdot}35}$$

or, Solubility of iodine in $CCl_4 = 88 \times 0{\cdot}35 = 30{\cdot}8$ gms/litre.

Henry's Law : This law states that the mass of a gas dissolved in given volume of a solvent is proportional to the pressure of the gas at constant temperature.

The volume (in CC) of a gas reduced to S. T. P. which is absorbed by 1 ml of a liquid is known as *solubility coefficient.* The volume of a gas reduced to S.T.P. which is absorbed by 1 cc of a liquid under latm pressure is known as *absorption coefficient.*

$$\text{Absorption coefficient} = \text{solubility coefficient} \times \frac{273}{T}.$$

Solved problem :

0·06 gm of oxygen dissolves in 1 litre of water at N. T. P. Calculate the weight of the gas that would get dissolved in 5 litres of water at 5 atm pressure and 0°C. *Bombay.* U. *I. Sc. 1976.*

We know from the Henry's law that mass of gas dissolved $\propto$ pressure of gas or $\frac{\text{mass of gas}}{\text{pressure of gas}} = \text{constant.}$

1 litre water at O°C and 1 atm pressure contains 0·06 gm oxygen.

∴ 5 „ „ „ „ „ „ contain $0{\cdot}06 \times 5 = 0{\cdot}3$ „

Mass of gas = 0·3 gm, pressure = 1 atm.

$\therefore \frac{0.3}{1} = \text{constant.}$ or, constant = 0·3.

Now, $\frac{\text{mass of gas per 5 litre water}}{5} = 0.3$

∴ mass of gas that would get dissolved in 5 litrewater
$= 0.3 \times 5 = 1.5$ gm.

Problems for practice :

Lowering of vapour pressure :

1. At 0°C the vapour pressure of purewater is 4·58 mm of Hg and that of a solution containing 8.8 gms of the solute per 100 gms of water is 4·559 mm of Hg. Calculate the molecular weight of the solute. *Calcutta.* U. *B. Sc. 1967*, '69. Ans. 343·88.

2. Pure and dry nitrogen gas is slowly bubbled through a solution of 2·25 gms of a non-volatile organic compound in 150 gms of benzene and then through pure benzene. The solution is found to be 2·154 gm lighter while pure benzene suffered a loss in weight of 0·0160 gm. Calculate the molecular weight of the dissolved substance. *Patna.* U. *1969 A.* Ans. 158·69.

3. When 2·47 gms of an ester were dissolved in 100 gms of a solvent of molecular weight 78, the vapour pressure of the solvent was lowered from 75·19 cms to 74·26 cms of Hg. Calculate the molecular weight of the ester. *Kerala.* U. *1971.* Ans. 153·8.

4. At 20°C the vapour pressure of ether is 442mm. When 6·1 gms of benzoic acid are dissolved in 50 gms of ether the vapour pressure falls to 410 mm. What is the molecular weight of benzoic acid ? *Nagpur* ; *Calcutta* ; *Punjab 1971.* Ans. 115·7.

5. A current of dry air is passed through a solution containing 5 gms of phenol in 50 gms of water and through pure water. If the loss in the weight of former is 1·85 gm and of latter is 0·036 gm. Calculate the molecular weight of phenol. *Ravisankar.* U. *B. Sc. 1973.* Ans. 92·93.

6. At 20°C, vapour pressure of ether (mol. wt=74) is 442 mm Hg. A dilute solution of an organic substance containing 6·5g of the said substance in 50g. of ether has a vapour pressure of 410 mm Hg at the same temperature. Calculate the molecular weight of the substance. *Calcutta. U. B. Sc. 1980.* Ans. 132·8.

7. The Vapour pressure of a 2·1% aqueous solution of a non electrolyte at 100°C is 755 mm. Calculate the molecular weight of the solute. *Bombay. U. I. Sc. 1971.* Ans. 57·456.

8. An aqueous solution (density=1·02) contains 5 gms of a solute per litre. The vapour pressure of water at 50°C is 92·17 mm and that of solution is 92·02 mm. Calculate the molecular weight of the solute. *Magadh.* U. *1971*A. Ans. 54·13.

9. Calculate with Raoult's law's help the molecular weight of a non volatile organic solute, 10 gms of which when dissolved in 100 gms of diethyl ether (mol wt=74) lowers its vapour pressure from 442·2 mm to 426·2 mm at 20°C. *Calcutta.* U. *B. Sc. 1972.* Ans. 97·1175.

10. A solution containing 25 gms of a sugar per 500 gms of water has a vapour pressure of 18·06 mm at a certain temperature. If the vapour pressure of pure water at the same temperature be 18·15 mm., calculate the molecular wt of the sugar. *Calcutta.* U. *B. Sc. 1973.* Ans. 182·773.

11. 13 gms of any solute is dissolved in 100 gm water. Vapour pressure of the solution at 28°C is 27·371 mm. If vapour pressure of water at that temperature is 28·065 mm., calculate the molecular weight of the solute. *L. N. M.* U. (*Bihar*) *1973A.* Ans. 94·6.

12. 3·5 gms of a non-volatile solid when dissolved in 100 gm water lower its vapour pressure from 2365 mm to 2288 mm mercury. Determine the molecular weight of the substance. *Calcutta.* U. *B. Sc. 1974.* Ans. 21·2.

13. The vapour pressure of pure water at 0°C is 4·579 mm of Hg. A solution of lactose (8·45 gm in 100 gms of water) has

a vapour pressure of 4·559 mm at the same temperature. Calculate the molecular weight of lactose. *I. I. T. 1976.*

Ans. 348·2.

Elevation of boiling point :

14. When 1·8 gm of a non volatile compound is dissolved in 25 gms of acetone, the solution boils at 56·86°C which pure acetone boils at 56·38°C under the same atmospheric pressure. Calculate the molecular weight of the compound. The molal elevation constant for acetone is 1·72°. *Punjab.* U. *1970.*

Ans. 258.

15. 1·19 gm of a substance dissolved in 35 gm of ether raised the boiling point of ether by 0·296°C. Calculate the molecular weight of the substance. The molecular elevation is 22·2°C for 100 gm of ether. *Ravisankar.* U. *B. Sc. 1973.*

Ans. 89·25.

16. A solution of 0·564 gm of a compound in 8·6 gm of acetone, boils at 56·75°C. The boiling point of pure acetone is 56·38°C. If the molecular elevation constant of acetone is 1·67°/1000 gm what is the molecular weight of the compound? *Ravisankar.* U. *B. Sc. 1978.*

Ans. 296.

17. A solution containing 0·5 gm of a substance dissolved in 42 gms of a volatile solvent (b. p. 10°C) boils at 80·175°C that the latent heat of vaporisation of the solvent is 94 cals per gm., calculate the molecular weight of the substance. *Madurai.* U. *1969.*

Ans. 180·4.

18. A solution of 3·795 gm sulphur in 100 gms of carbon-disulphide (b. p. 46·30°C ; ΔH vap=7400 cals/mole) boils at 46·66°C. What is the formula of sulphur molecule in the solution? *Jadabpur.* U. (*West Bengal*) *B. Sc. 1970.* *A*ns. S_8.

Depression of freezing point :

19. 0·60 gm of a substance dissolved in 50 gms of water lowered its freezing point by 0·37°C. Find the molecular weight

of the substance. The molecular depression is 18·5°C for 100 gms of water. *Ravisankar.* U. *1969*. Ans. 60.

20. The molecular weight of phenol is 94 and that of cane sugar is 342. A depression of 0·096°C is produced in the freezing point of water when 0·237 gm of phenol is dissolved in 50 gms of water. What amount of sugar dissolved in 40 gms of water will cause the same depression of freezing point ? *Bihar.* U. *1969A*. Ans. 0·0689 gm.

21. A solution of 0·911 gm of a substance in 50 gms of benzene showed a depression in freezing point 0·603°. Calculate the molecular weight of the substance if $K_f = 5{\cdot}12$ (per 1000 gms of solvent). *Calcutta.* U. *B. Sc. 1970.* Ans. 154·703.

22. Calculate the freezing point of a 2% solution of sodium chloride, assuming it to be 90% dissociated (Na = 23, Cl = 35·5) (K_{1000} for water = 1·85°C). *Magadh.* U. *1970A.* Ans. 1·201°C.

23. When 0·25 gm of a substance was dissolved in 100 gms of water the freezing point of the latter was lowered by 0·43°C. Find the molecular weight of the substance (molecular depression for 100 gms of water is 18·5°C). *Meerut.* U. *1971.* Ans. 107·56.

24. The solution obtained by dissolving 6 gms of sodium chloride in 100 gms of water freezes at −3·1°C. Calculate the degree of dissociation of sodium chloride, K_f for water (1000 gm) being 1·86. *Magadh.* U. *1967A* ; *Patna.* U. *1973A.*

Ans. 0·62 or 62%.

25. 2 gms of a substance when dissolved in 70 gms of water lower the freezing point by 0·15°C. Calculate the mol. wt. of the substance ($K_{100} = 18{\cdot}6$). U. *P. 1978S.* Ans. 354·3.

26. On dissolving a substance of mol. wt. 154·7 in 50 gm benzene, the freezing point depression was found as 0·603°C. Calculate the weight of the substance dissolved, the molar freezing point depression constant of benzene (per 1000 gm) being 5·12°C. *Calcutta.* U. *B. Sc. 1979.* Ans. 0·911 gm.

27. A soln. containing 1 gm of a non-volatile solute per 100 gms of water freezes at −0·103°C. Calculate the mol. wt. of the

solute. [Cryoscopic constant for water = 1·86]. *Calcutta.* U. *B. Sc.* (*A*) *1979.* Ans. 180·58.

28. 5 gm substance dissolved in 50 gm water lowered the freezing point by 1·2°C. Calculate the molecular weight of the substance. The molecular depression for water is 18·5°C.
Ravisankar. U. *B. Sc. 1975.* Ans. 1541·66.

Osmotic pressure :

29. Calculate the osmotic pressure at 25°C of a solution containing 8·96 gms of a compound of molecular weight 286 dissolved in 100 ml water (R = 82·06 ml atm deg^{-1} $mole^{-1}$)
Calcutta. U. *B.* Sc. *1973.* Ans. 7·661 atms.

30. A solution containing 1 gm of a substance per 100 cc has an osmotic pressure of 309 cms of Hg at 15°C. Calculate the molecular weight of the substance. (R = 0·082 lit. atm deg^{-1} $mole^{-1}$). *Calcutta.* U. *B.* Sc. *1976.* Ans. 236·16.

31. Calculate the osmotic pressure of N/10 solution of cane sugar at 0°C. *I. I. T. 1976.* Ans. 2·24 atms.

32. Calculate the osmotic pressure of 5% solution of cane sugar at 15°C. *Allahabad.* U ; *Rajasthan.* U. *1970.*
Ans. 3·453 atms.

33. The osmotic pressure of a soln containing 3 gms of a solute per litre is 0·41 atm. at 27°C. Calculate the mol. wt. of the solute. *Calcutta. U. B. Sc.*(*A*) *1980.* Ans. 180·22.

34. 40 gms of a substance dissolved in 600 ml water showed an osmotic pressure of 8·2 atm at 0°C. If R is 0·082 lit. atm/deg ; find the molecular weight of the substance. *Bombay.* U. *1971.*
Ans. 182.

35. If a 2% solution of sugar has an osmotic pressure of 1016 mm at 15°C what is the molecular weight of sugar ?
Patna. U. *1975A.* Ans. 353·3.

36. A solution containing 20 gms of a substance in a litre of solution has an osmotic pressure of 3 atmosphere at 27°C. Calculate the molecular wt. of the substance. (R = 0·082 lit. atm. deg^{-1} $mole^{-1}$). *C.* U. *B. Sc.* (*New*) *1980.* Ans. 164.

37. Calculate the osmotic pressure of a solution containing 0·40% urea (mol wt = 60) together with 3·42% sugar (mol wt = 342) at 27°C. *Magadh.* U. 1970*A*. Ans. 2·05 atms.

38. Calculate the osmotic pressure of N/10 NaCl soln at at 27°C, assuming the salt is 90% dissociated at this dilution.
Mysore. U. 1970. Ans. 4·6797 atms.

39. De Vries found that 3·42% solution of sugar was isotonic with a 5·96% soln of raffinose. Calculate the molecular weight of raffinose. *Patna.* U. 1974. Ans. 596.

40. A 6% glucose soln is isotonic with 2% soln of an organic compound 'Y'. Determine mol. wt. of 'Y'. *Ravisankar.* U. *B. Sc.* 1976. Ans. 60.

41. A 5% soln of cane sugar is isotonic with 0·877% soln of urea. Find the molecular weight of urea. Mol. wt. of cane sugar = 342. *Ravisankar.* U. 1974, *Patna.* U. 1974. Ans. 59·98.

Distribution law

42. 2 gms of iodine is dissolved in a mixture containing equal volumes of water and carbon disulphide. The distribution coefficient of iodine in carbon disulphide and water is 410. Calculate the mass of iodine in water. U. *P. I.* Sc. 1978.
Ans. 0.00487 gm.

43. A solution of 5 gms of iodine in CS_2 was shaken with the same valume of water. What will be the amount of iodine in water ? Distribution coefficient = 420. U. *P. I.* Sc. *1978S.*
Ans. 0·0119 gm.

44. 5g of a substance dissolved in 100 cc of water was extracted with ether in two different ways as follows :

(i) In the first case 100 cc of the aqueous solution was extracted with 100 cc of ether and the ether evaporated off. (ii) In the second case 100 cc of the aqueous solution was extracted twice with 50 cc of ether each time and the combined 100 cc of ether evaporated off. (1) Which of the two methods of extraction gives a better yield of the substance. (2) If the distribution coefficient of the substance between water and ether is 1/4 at room temperature, calculate the amount of th substance recovered in each of the two cases. *I. S. C. E.* 1979.

[Soln. K = distribution coefficient of the substance

$= \frac{\text{concn of the substance in water}}{\text{concn of the substance in ether}} = \frac{1}{4}$ at room temperature.

(1) When 100 cc ether used for extraction, let S_e gm of the substance go into ether layer and S_w gm be left in aqueous layer.

So, $K = \frac{1}{4} = \frac{S_w/100}{S_e/100}$ or, $\frac{S_e}{S_w} = 4$ or, $\frac{S_e}{S_e + S_w} = \frac{4}{4+1} = \frac{4}{5}$.

This indicates 100 cc ether separate $\frac{4}{5}$ th or 80% (5 parts contain 4 part substance ; 100 parts contain $\frac{4}{5} \times 100 = 80$ part substance) of the substance initially present. (2) Let us now use 100 cc ether in two successive extractions employing 50 cc. each time. Then in the lst stage of operation,

$\frac{S_w/100}{S_e/50} = \frac{1}{4}$ or, $\frac{S_w}{S_e + S_w} = \frac{2}{3}$ i.e., in the 1st extraction 2/3 rd or 66·7% substance is extracted. ∴ 1/3 rd of the initial amount is still retained in aqueous medium. In the 2nd extraction using 50 cc ether, further 2/3 rd of 1/3 rd i.e., 2/9 th of the initial amount is extracted. Hence, in two extractions using 100 cc ether in total, $\frac{2}{3} + \frac{2}{9} = \frac{8}{9}$ or 88·9% of the initial amt. of the substance is extracted. So, a two stage extraction is more efficient. Now, amount of the substance recovered in the one operation $= 80\% = \frac{80}{100} \times 5 = 4$g.

Amount of the substance recovered in a two stage extraction $= 88{\cdot}9\% = \frac{88{\cdot}9}{100} \times 5 = 4{\cdot}445$ g.]

45. 1·82 gm of an organic acid (eq wt 40) was dissolved in a mixture of 200 cc of toluene and 100 cc of distilled water. 25 cc of the aqueous layer was found to require 16·3 cc of N/2 NaOH solution for neutralisation. Calculate the distribution ratio of the organic acid between water and toluene, assuming the acid behaves as a normal molecule in both the solvents. *Ans.* 5·054.

46. A mixture of water and bromobenzene boils at 95·2°C. The vapour pressure of water at that temperature is 641 mm. The distillate contains 61·83% w/w bromobenzene. Calculate the mol. wt. of bromobenzene. *Calcutta. U. B. Sc. 1980.*

[Hints. Vide steam distillation.

Let $p_{\text{bromobenzene}} = p_b$; $p_{\text{watervapour}} = p_w$; $n_{\text{bromobenzene}} = n_b$; $n_{\text{water vapour}} = n_w$; mol. wt. of bromobenzene $= M_b$ and mol. wt. of water vapour $= M_w$.

$$\frac{p_b}{p_w} = \frac{n_b}{n_e} \quad \text{or,} \quad \frac{p_b}{p_w} = \frac{W_b/M_b}{W_w/M_w} \quad \text{or,} \quad M_b = \frac{W_b \times p_w \times M_w}{p_b \times W_w}$$

$$= \frac{61{\cdot}831 \times 641 \times 18}{(760-641) \times (100-61{\cdot}83)} = 151{\cdot}8.$$

$\because \quad p_b + p_w = 760$ mm ; $W_b + W_w = 100$.]

47. The distribution coefficient of iodine between CCl_4 and water is 61·08 at 31°C. What volume of the CCl_4 layer at 31°C would contain 5·32 gms of iodine, when 6·1 gms of iodine are dissolved in 1000 cc of a mixture of CCl_4 and water? (Assume that the volumes of CCl_4 and water are equal.)

Ans. 445·70 cc.

Henry's law :

48. The solubility coefficient of oxygeen is 0·05 at 0°C. What weight of the gas under 12 atm pressure will be dissolved in 25 litres of water at 0°C? *Ans.* 21·43 gms.

49. 1 litre of liquid at 27°C dissolves 84 ml of a gas at 2 atm pressure. What are the solubility coefficient and absorption coefficient of the gas? *Ans.* 0·084 ml ; 0·076 ml.

50. The solubility of an inert gas at various pressures is measured at 25°C. The following experimental results are obtained.

Pressure of gas (in atm)	32·1	65·0	80·0	110·0.
Mass of gas (in gm)	0·0033	0·0066	0·0081	0·0112.

Show that the inert gas obeys the Henry's law of solubility.

CHAPTER 13

Problems on Atomic structure

Solved problems :

1. Fill up the blanks :— *Patna.* U. 1970.

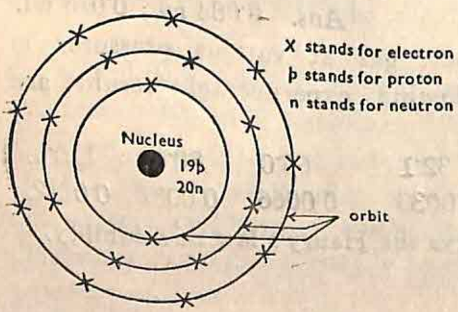
Element	At wt	No of neutrons	No of protons	No of electrons	At No
Na	23	....	11	...	...
P	...	16	...	...	15

Ans.

Element	At wt	No of neutrons	No of protons	No of electrons	At No
Na	23	$23-11=12$	11	11	11
P	31	16	15	15	15

2. The atomic number of an atom is 19 and its atomic weight is 39. Show the 'atomic structure' of this element giving the composition of the nucleus and the distribution of the electrons in its different orbits. *Patna.* U. 1974*A.*

Ans. *Atomic* number of the atom$=19$ ∴ number of protons $=$number of electrons$=19$ ∵ atomic weight$=39$ ∴ number of neutrons$=39-19=20$. Distribution of the electrons in the different orbits of the atom is therefore 2, 8, 9 according to the $2n^2$ rule. Where, n represents path number and $2n^2$ represents total number of mobil electrons in the corresponding path (orbit). Considering all these facts the atomic structure of this element is drawn below.



Using Aufbau principle and considering subshell idea, electronic configuration is as follows :—

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$. s, p, d represent different subshells.

3. The number of protons, neutrons and orbital electrons in particles *A* – E are given :— *West Bengal H. S.* 1976.

	Proton	Neutron	Electron
A—	11—	12—	10
B—	9—	10—	10
C—	17—	18—	17
D—	17—	20—	17
E—	10—	10—	10

From these particles choose :—(i) an ion ; (ii) a cation ; (iii) an inert gas atom ; (iv) a pair of isotopes ; (v) two particles which may form an electrovalent bond and (vi) an atom that can form an acidic hydride.

Ans. (i) B is an ion because there is a difference between number of electrons and number of protons in B ; (ii) *A* is a cation because number of protons is greater than that of number of electrons in *A* ; (iii) E is an inert gas atom because distribution of electrons in E is similar to inert structure (Viz. 2, 8) arrangement ; (iv) C and D are isotopes in pair. They have same atomic number (number of protons) but different neutron number ; (v) A and B form an electrovalent compound with the help of electrostatic like force as they are two opposite types of charged particles and (vi) C atom can form an acidic hydride because it easily shares one electron to hydrogen atom.

4. Name the three fundamental particles which make up the structure of the atom of an element. How are the atomic number and atomic weight related to these three fundamental particles ? Give the number of these particles in chlorine—35 and chlorine —37 (atomic number of chlorine = 17) and explain your answer.

West Bengal H. S. C. 1978.

Naming : Proton, electron and neutron are the three fundamental particles.

At. No : Number of extranuclear electrons or number of protons in nucleus determines atomic number. At. wt : number of protons and neutrons in nucleus determines atomic weight.

In Cl^{35}, number of electrons = 17, number of protons = 17 and number of neutrons = 18.

Atom is electrically neutral, hence 17 protons neutralise 17 electrons. Hence, number of neutrons is 18 to make Cl^{35} as the atomic weight consists of proton and neutron.

In Cl^{37}, number of electrons = 17, number of protons = 17 and number of neutrons = 20.

Atom is electrically neutral, hence 17 protons neutralise 17 electrons. Hence, number of neutrons is 20 to make Cl^{37} as the atomic weight consists of proton and neutron.

Problems for practice :

1. The nucleus of an atom of an element consists of twelve neutrons and eleven protons. What is the atomic weight and the electrovalency of the element ? *Punjab*. U. *I*. *Sc*. 1962.

Ans. 23, monovalent electronegative.

2. What is the atomic number of an element having atomic weight 60 and containing 30 neutrons ? *All India H*. S. 1970.

Ans. 30.

3. The atomic number of phosphorous is 15 and its atomic weight is 31. Show the 'atomic structure' of this element giving the composition of the nucleus and the distribution of the electrons in its different orbits. *Bhagalpur*. U. 1974*A*.

Ans. 15*e*, 15*p*, 16*n* ; 2, 8, 5.

4. The number of protons and neutrons in the nucleus of an element is 11 and 12 respectively. What will be the atomic structure of the element ? Write also the name of the element. *Patna*. U. 1975 *A*. Ans. 11p, 11e, 12n, at. wt. = 23 ; 2, 8, 1 ; sodium.

5. The neucleus of the atom of an element contains 8 protons and 8 neutrons. What is the element ? What is its valency and why ? What are the number of atoms in 8 gms of the element ? *West Bengal H. S. Comp. 1975*.

Ans. Oxygen, 2, $30{\cdot}115 \times 10^{22}$.

6. Write simply "Yes" or "No" against the statement as below :—(a) $Fe^{3+} + e \rightarrow Fe^{2+}$ is an oxidation reaction ; (b) cathode rays are electromagnetic radiations ; (c) an atom is electrically neutral ; (d) charge of an electron is equal to $4{\cdot}83 \times 10^{-10}$ e. s. u ; (e) when Be—metal is bombarded with α—particles, protons are produced ; (f) molecular and equivalent weights are whole numbers ; (g) Sodium chloride and methane are electrovalent compounds and (h) vapour density of ammonium chloride is experimentally found to be normal.

Ranchi . U. *1976A.* Ans. (a) No, (b) Yes, (c) Yes, (d) Yes, (e) No, (f) No, (g) No and (h) No.

7. State with reasons whether the following statements are true or false (attempt any four) :—*West Bengal H. S. C. 1978.*

(a) Sodium chloride is a covalent compound. (b) Isotopes of the same element have different chemical properties. (c) The diatomic molecule AB will be polar, when A and B are different elements. (d) Electrolysis is possible only with electro-valent compounds and not with covalent compounds. (e) Avogadro's number can be determined by knowing the charge of the electron. (f) Sodium Chloride is more soluble in a hydrochloric acid solution than in water.

Ans. (a) False : Sodium transfers its one extra—nuclear electron to the outermost orbit of Cl containing 7 electrons to complete the octet. Hence Na loses one electron, Cl gains one. Na and Cl thus form ionic bond.

(b) False : Chemical properties depend on the electrons in the outer most shell which remain the same in isotopes.

(c) True : As different elements have different degrees of electronegativities, the diatomic molecule AB will be polar when A and B are different elements.

(d) True : Electrovalent compounds loosely bound bonds, ionise easily and hence undergo electrolysis. On the other hand co-valent compounds firmly bound bonds, do not ionise and hence question of electrolysis does not arise.

(e) True : One Faraday (96,500 coulombs) liberates Avogadro's number of H^+ ions. Therefore 96,500 coulombs = Avogadro's number of electrons.

or, 96500 coulombs = Avogadro's number × charge of electron

$$\text{or, charge of electron} = \frac{96500}{\text{Avogadro's number}}$$

$$\therefore \text{ Avogadro's number} = \frac{96500}{\text{Charge of electron}}.$$

Hence Avogadro's number can be determined by knowing the charge of the electron.

(f) False : Sodium chloride is less soluble in a hydrochloric acid solution than in water because of common ion effect.

8. Calculate the energy released when 0·025 gm of matter is destroyed. *Hyderabad I. Sc. 1977.*

Ans. Mass of the matter = 0·025 gm ; C = velocity of light = 3×10^{10} cms/sec. Now, $E = mc^2 = 0{\cdot}025 \times (3 \times 10^{10})^2 = 225 \times 10^{17}$ ergs.

$E = mc^2$ is the Einstein's law of mass energy equivalence.

9. Give the electronic configuration of the carbon atom. *W. B. H. S. C. 1978.* Ans. 6*n*, 6*p*, 6*e* ($1s^2, 2s^2, 2p^2$).

10. Calculate the number of electrons transferred from sodium to chlorine during the formation of 58·5 gms of sodium chloride. *Indian School Certificate Examination, 1978.* Ans. 1.

11. The table shows the mass numbers, the number of neutrons and the ionization energies in electron volts of four elements A, B, C and D. *Indian School Certificate Examination, 1978.*

	A	B	C	D
Mass number	23	20	12	35
Neutrons in nucleus	12	10	6	18
Ionization energies	5·1e.v.	21·6e.v.	11e.v.	13e.v.

(a) Write down the atomic number of the element D. (b) "The electronic structure of the element A can be written down as $1s^2, 2s^2, 2p^6, 3s^1$. In the same way write down the structure of the element D." (c) Why is the second ionization energy of an atom always larger than the first ? (d) What will be the nature (ionic or covalent) of the compounds formed by :—(i) A and D ; (ii) C and D. (e) In a text-book it is stated that the atomic weight of chlorine is 35·5 rather than 35 or 37. How do you account for this ? (f) The atoms X and Y have the electronic configurations X, $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$; Y, $1s^2$, $2s^2$, $2p^4$. Write down the formula of the compound formed by X and Y. (g) Show on a labelled sketch the shapes and spatial distributions of all the orbitals of principal quantum number 2.

12. State the electronic configuration and valency of an element whose mass number is 39 and atomic number is 19. *W. B. J. E. E. 1977.* Ans $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$; 1.

13. Note down the number of electrons present in the outer most shell of the following elements : O, Al, P, Mn, Sn, Ne, Cl, Ag. *Ranchi.* U. *1978.*

14. Choose and write the correct answer in each case :

(a) As α—particle goes closer to the nucleus :—(i) the force of repulsion increases enormously, (ii) the force of repulsion decreases enormously, (iii) the force of repulsion does not show any change. (b) Atomic number of an element is equal to the number of—(i) electrons in its orbit, (ii) protons in its nucleus, (iii) neutrons in its nucleus. (c) An element has atomic weight of 23 and its atomic number is 11. Hence the number of neutrons in it will be—(i) 12, (ii) 23, (iii) 11. (d) If n denotes the number of orbits, then the maximum number of electrons that can exist in an orbit is given by—(i) n ; (ii) $2n^2$; (iii) n^3. (e) An electron will first of all occupy the—(i) s-orbital ; (ii) d-orbital ; (iii) p-orbital. (f) Outer most orbit of an inert gas contains :—(i) 8 electrons, (ii) 18 electrons ; (iii) 32 electrons. *Ranchi.* U. 1977.

15. (i) The total number of electrons in one molecule of carbon dioxide is (a) 22 (b) 44 (c) 66 (d) 88. (ii) The number of neutrons in dipositive zinc ion with mass number 70 is (a) 34 (b) 36 (c) 38 (d) 40. *I. I. T.* 1979.

16. Name the three fundamental particles which make up

the structure of the atom of an element. How are the atomic number and mass number related to these three fundamental particles ? An atom of an element contains 17 protons and 18 neutrons in its nucleus. What is its (i) atomic number, (ii) mass number ? How many electrons does the atom contain and how are the electrons arranged in the shells of the atom ? *W. B. H. S. C. 1979 (Voc).* Ans. electrons, protons and neutrons, number of protons ; number of protons+neutrons ; 17 ; 35 ; 17 ; 2, 8, 7 or $1s^2 2s^2 2p^6 3s^2 3p^5$.

17. The atomic number of an element is 35 and atomic weight of two of its isotopes are 79 and 81. Find out (1) the number of electrons in the outermost orbit (2) valency of the element (3) the number of neutrons and protons in the nuclei of the two isotopes. *P. M. T. Allahabad. 1970.*

Ans. 7, −1, 35, 44 & 35, 46.

18. Given the atomic number of element, which of the following can you find and which not ? (a) The number of electrons in the atom, (b) The atomic weight, (c) The number of isotopes, (d) The total positive charges on the nucleus, (e) The number of neutrons in the nucleus and (f) The number of protons in the nucleus. U*ttar Pradesh I. Sc.* 1970.

19. Write in brief about the atomic structure of fluorine and phosphorous. *Roorke Adn. T. E. 1976.*

20. Note down the electronic configurations of the following atoms :

Elements	Na	Ca	Cu	Xe	Ra
At. No.	11	20	30	54	88

Ranchi. U. 1979.

21. Calculate the wavelength associated with an electron (mass $9{\cdot}1 \times 10^{-31}$ kg) moving with a velocity of 10^3 m/sec. ($h = 6{\cdot}6 \times 10^{-34}$ kg m^2 sec^{-1}), *I. S. C. E.* 1979. Ans. $0{\cdot}725 \times 10^{-6}$m.

$\left[\text{Hints } \lambda = \frac{h}{mv}\right]$.

22. Find (i) the total number of neutrons ; (ii) the total mass of neutrons in 7 mg of ^{14}C. (Assume that mass of a neutron

=mass of hydrogen atom.) and (iii) the total number of electrons present in 18 ml of water. *I. I. T.* 1980.
Ans. (i)$24{\cdot}092 \times 10^{20}$; (ii) $24{\cdot}092 \times 10^{20}$ gms ; (iii) $6{\cdot}023 \times 10^{24}$.

24. Explain why dilute H_2SO_4 behaves as a stronger acid than conc. H_2SO_4. *W. B. J. E. E.* 1980. Ans. With the dilution of conc. H_2SO_4, heat is evolved. This heat breaks the O−H bond, so dil. acid contains more of H^+ ions than conc. H_2SO_4. Hence, dil H_2SO_4 behaves as a stronger acid than conc. H_2SO_4.

25. (a) Show the distribution of electrons in different shells and subshells of three elements A, B and C having atomic numbers 1, 11 and 17 respectively. State the nature of valencies shown by a compound of B and C and a compound of A and C. Indicate the groups in the periodic table to which B and C can be included. (b) Account for the following :—(i) Atomic weight of an element is fractional, but the atomic mass is a whole number. (ii) Water has boiling point much higher than those of hydrides of other elements of the same group as oxygen. *W. B. J. E. E.* 1980. Ans. (a) K($1s^1$) ; K($1s^2$) L ($2s^2 2p^6$) M ($3s^1$) ; K ($1s^2$) L ($2s^2 2p^6$) M ($3s^2 3p^5$) ; electrovalency ; co-valency ; I & VII. (b) (i) atomic weight is fractional because the element contains isotopes in different proportions. Atomic wt is the mean of the wts of these isotopes. As atomic mass is equal to the no of protons and neutrons both are complete numbers, it is whole number. (ii) Due to covalent linkage and hydrogen bonding.

26. The electron arrangement of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ (i) What is its atomic number ? (ii) If its atomic mass is 27 state the number of each type of particles present in its nucleus. (iii) What is possible valency ? (iv) What is its position in the periodic table ? Ans. (i) 13 ; (ii) 13p, 14*n* ; (iii) 3 and (iv) IIIA. W. *B. H. S. C. 1980.*

27. (a) What are the similarities between the solar system and the atomic structure ? What are the dissimilarities ?

(b) What do you understand by the statement that the mass number of chlorine is 35 ? (c) Which of the following statements are correct ? Rectify the incorrect statements. (i) There are protons and electrons in an atomic nucleus. (ii) Neutrons are positively charged particles. (iii) Atomic numbers of isotopes are different but their mass numbers are equal. (iv) Two electrons revolve in the orbit of the helium atom.

W. *B. H. S. C. (Voc) 1980.*

28. Calculate the momentum of a particle which has a de Broglie wavelength of 1°A (i.e. 10^{-10} m) ; $h = 6{\cdot}6 \times 10^{-34}$ Kg m^2 sec^{-1}. *I. S. C. E. 1980.* Ans. $6{\cdot}6 \times 10^{-24}$ Kg m sec^{-1}.

29. Calculate the bond order of He_2^+, O_2 and N_2 molecules. *I. S. C. E. 1980.* Ans. $\frac{1}{2}$, 2, 3.

30. (a) Chlorine has two types of atoms of atomic masses 35 and 37 respectively. The atomic number of chlorine is 17. State the composition of their nuclei and their electronic configurations. (b) What is the difference between 2O and O_2 ?

W. B J. E. E. (Polytechnic) 1980.

Ans. (a) 17p, 17e, 18n ; 17p, 17e, 20n ; 2, 8, 7 ; $1s^2 2s^2 2p^6 3s^2 3p^5$ (b) 2 oxygen atoms ; diatomic oxygen molecule.

CHAPTER 14

Balancing a Chemical Equation

Oxidation number method :

When a substance is oxidised its oxidation number (O.N.) gets increased whereas when the substance is reduced its oxidation number gets decreased. When a substance is oxidised, at the same time another substance is reduced. The change in oxidation number is explained by some examples. Before giving examples some rules are written bellow which will be helpful to note the change.

Rules :

1. Oxidation number of all elements in free state is considered to be zero.

2. In a compound oxidation number of hydrogen and oxygen is considered +1 and −2 respectively. '+' sign indicates increase in oxidation no where as "−" sign indicates decrease in O. N.

3. Sum of the oxidation number of all the elements present in a compound is taken as zero.

Note: In hydrides like NaH, oxidation number of hydrogen is -1. In peroxides like Na_2O_2, H_2O_2, oxidation number of oxygen is -1. In SbH_3, Sb is negative otherwise a metal atom is usually positive. In F_2O, oxidation number of oxygen is $+2$.

Examples:

1. Find the oxidation number of Mn in $KMnO_4$ or MnO_4^- and C in C_2H_4. *West Bengal H. S. C.* 1978 ; U. P. 1977, '78.

(a) Let the oxidation number of Mn be X. Oxidation number of one atom of $K = +1$; oxidation number of 4 atoms of oxygen $= -2 \times 4 = -8$. $\therefore$ $1 + X - 8 = 0$ (Vide. rule 3). $\therefore$ $X = +7$. Oxidation number of Mn in $KMnO_4$ is therefore $+7$. (b) Let the oxidation number of C be X. Oxidation number of 4 hydrogen atoms $= 4 \times (+1) = +4$. $\therefore$ $2X + 4 = 0$ or, $2X = -4$ $\therefore$ $X = -2$. Oxidation number of C in C_2H_4 is therefore -2.

2. Find the oxidation number of C in (a) CH_4 ; (b) C_2H_2 and (c) C_6H_6.

Let the oxidation number of C be X.

(a) Oxidation number of 4 hydrogen atoms $= +4$.

Now, $X + 4 = 0$ $\therefore$ $X = -4$.

(b) Oxidation number of 2 hydrogen atoms $= +2$.

Now, $2X + 2 = 0$ $\therefore$ $X = -1$.

(c) Oxidation number of 6 hydrogen atoms $= +6$.

Now, $6X + 6 = 0$ $\therefore$ $X = -1$.

3. Find out the oxidation number of Cr in (a) $K_2Cr_2O_7$ and (b) K_2CrO_4. *U. P. 1978.*

Let the oxidation number of $Cr = X$.

(a) Oxidation number of 2 potassium atoms $= 2(+1) = +2$ and oxidation number of 7 oxygen atoms $= 7(-2) = -14$.

Now, $2 + 2X - 14 = 0$ $\therefore$ $X = +6$.

(b) Oxidation number of 4 oxygen atoms $= 4(-2) = -8$.

Now, $2 + X - 8 = 0$ $\therefore$ $X = +6$.

4. Find the change in the value of the oxidation number of C, when CO_2 is oxidised to H_2CO_3.

Oxidation number of C in $\overset{+4}{C}\overset{-4}{O_2} = +4$.

Oxidation number of C in $\overset{+2}{H_2}\overset{+4}{C}\overset{-6}{O_3} = +4$.

$\therefore$ change in the value of oxidation number of $C = (+4) - (+4) = 0$.

5. Find the increase in the value of the oxidation number of S, when H_2S is oxidised to (a) S and (b) SO_2.

(a) Oxidation number of S in $\overset{+2}{H_2}\overset{-2}{S} = -2$; oxidation no of S in free state $= 0$ (vide. rule 1.). So, increase in the value of the oxidation number of S, when H_2S is oxidised to $S = 0 - (-2) = 2$.

(b) Oxidation number of S in $\overset{+4}{S}\overset{-4}{O_2} = +4$; so, increase in the value of the oxidation number of S, when H_2S is oxidised to $SO_2 = (+4) - (-2) = 6$.

6. Find the decrease in the value of the oxidation number of nitrogen when HNO_3 is reduced to (a) NH_3 and (b) N_2H_4.

(a) Oxidation number of N in $\overset{+1}{H}\overset{+5}{N}\overset{-6}{O_3} = +5$; oxidation number of N in $\overset{-3}{N}\overset{+3}{H_3} = -3$.

$\therefore$ decrease in oxidation number $= 5 - (-3) = 8$.

(b) oxidation number of N in $\overset{-4}{N_2}\overset{+4}{H_4} = -2$.

$\therefore$ decrease in oxidation number $= 5 - (-2) = 7$.

Method of balancing :

When a reaction occurs in between an oxidising agent and a reducing agent, the oxidising agent gets reduced and its one of the elements' oxidation number decreases, on the other hand the reducing agent gets oxidised and the oxidation number of of its one of the elements increases. Now, find out decrease and increase in oxidation number in 1st and 2nd case respectively. Multiply the value of increase in oxidation number of the reducing agent with the oxidising agent and the value of decrease in oxidation number of oxidising agent with the reducing agent.

Thus left hand side of the chemical equation is obtained. From the left hand side, the right hand side of the equation can easily be written,

Examples :

1. Stannous chloride reduces ferric chloride to ferrous chloride and is itself oxidised to stannic chloride.

Equation of this reaction is as follows :—

$\overset{+3}{Fe}Cl_3 + \overset{+2}{Sn}Cl_2 \rightarrow \overset{+2}{Fe}Cl_2 + \overset{+4}{Sn}Cl_4$.

In this reaction, oxidation number of iron decreases from +3 to +2 and oxidation number of tin increases from +2 to +4.

i.e., increase in oxidation number of tin=2 and decrease in oxidation number of iron=1.

∴ We can write, $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$.

The above equation is thus balanced.

2. When SO_2 is passed into $KMnO_4$ solution, the former (SO_2) is oxidised into H_2SO_4, and the latter ($KMnO_4$) is reduced to $MnSO_4$.

Equation of this reaction is written as follows :

$X\overset{+4}{S}O_2 + YKM\overset{+7}{n}O_4 \rightarrow H_2\overset{+6}{S}O_4 + K_2SO_4 + \overset{+2}{Mn}SO_4$

X = decrease in O.N of Mn = 7 − 2 = 5 ; Y = increase in O.N. of S = 6 − 4 = 2. ∴ L.H.S. of the equation = $5SO_2 + 2KMnO_4$

To write R.H.S. of the equation :

2K from the L.H.S. give one molecule of K_2SO_4.
2Mn „ „ „ two molecules " $MnSO_4$.
$5SO_2$ „ „ „ 5 „ " H_2SO_4.

Out of 5 molecules of H_2SO_4, one molecule is used for the production of K_2SO_4 and two molecules, used for the production of $MnSO_4$. ∴ residual number of molecules of H_2SO_4 = 5 − 1 − 2 = 2. So, the equation is re-written as :

$5SO_2 + 2KMnO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$.

The above equation is not balanced because there are 4 hydrogen atoms in the R. H. S. of the equation whereas there is nil number of atoms of hydrogen in L. H. S.

To make equality in the number of atoms of hydrogen in the both sides of the equation, $2H_2O$ is added in the L. H. S.

The equation is again written as :

$5SO_2+2KMnO_4+2H_2O \rightarrow K_2SO_4+2MnSO_4+2H_2SO_4$.

Now, see the total number of atoms of oxygen in the both sides of the equation. It is twenty in each side. Hence, the above equation is balanced one.

3. When ferrous sulphate is treated with HNO_3 in presence of H_2SO_4, it is oxidised into ferric sulphate and nitric acid is reduced to NO.

Equation of the reaction can be written as

$$X\overset{+2}{Fe}SO_4+YH\overset{+5}{N}O_3=\overset{+3}{Fe}_2(SO_4)_3+\overset{+2}{N}O+\ldots$$

X = decrease in O. N. of nitrogen $=5-2=3$; Y = increase in O.N. of Fe $=3-2=1$. $\therefore$ L.H.S. of the equation $=3FeSO_4+HNO_3$. $3FeSO_4$ give $\frac{3}{2}\,Fe_2(SO_4)_3$. $\because$ number of molecules should be whole number $\therefore$ to make $\frac{3}{2}$ as whole number multiply 2 with the left hand side of the equation.

So, L. H. S. of the equation $=6FeSO_4+2HNO_3$.

Now, 6*Fe* from the L. H. S. produce $3Fe_2(SO_4)_3$;

2N ” ” ” ” 2NO.

$\therefore$ equation is written as $6FeSO_4+2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO +$

To equal the number of SO_4 radicals in the both sides of the above equation, $3H_2SO_4$ are added in the L. H.S.

Again, 8H from the L. H.S. produce $4H_2O$. $\therefore$ the equation can be written as $6FeSO_4+2HNO_3+3H_2SO_4=3Fe_2(SO_4)_3+2NO+4H_2O$.

Whether the equation is balanced, checked by the number of oxygen atoms in the both sides of the equation. The number is 42 in each side.

4. H_2S reduces orange $K_2Cr_2O_7$ solution, acidified with

dilute H_2SO_4, to green $Cr_2(SO_4)_3$ and K_2SO_4, S and H_2O are also produced in the reaction.

Equation of the reaction is written below.

$XH_2S^{-2}+K_2\overset{+6}{Cr_2}O_7 \rightarrow S^0+K_2SO_4+Cr_2^{+3}(SO_4)_3+H_2O$

X = decrease in O.N. of Cr = 6 − 3 = 3.

Here, one molecule of $K_2Cr_2O_7$ contains 2Cr(+6) atoms which is equal to increase in O.N. of S. That is why $K_2Cr_2O_7$ is not multiplied with 2.

The equation is therefore $3H_2S+K_2Cr_2O_7 \rightarrow S+K_2SO_4+Cr_2(SO_4)_3+H_2O$. $3H_2S$ molecules produce 3S atoms; 2K atoms produce one K_2SO_4 molecule and 2Cr atoms produce one $Cr_2(SO_4)_3$ molecule. As there are $4SO_4$ radicals in the R. H.S. of the equation, $4H_2SO_4$ molecules are added in the L. H. S.

The equation is re-written as

$3H_2S+K_2Cr_2O_7+4H_2SO_4 \rightarrow 3S+K_2SO_4+Cr_2(SO_4)_3+H_2O$.

14H atoms from L. H. S. produce $7H_2O$ molecules.

∴ the equation is $3H_2S+K_2Cr_2O_7+4H_2SO_4 \rightarrow 3S+K_2SO_4+Cr_2(SO_4)_3+7H_2O$.

Whether the equation is balanced, checked by the number of oxygen atoms in the both sides of the equation. The number is 23 in each side.

5. Copper dissolves in moderately concentrated HNO_3 to form $Cu(NO_3)_2$, NO and H_2O.

HNO_3 at first oxidises Cu into CuO and CuO reacts later with excess of HNO_3 to produce $Cu(NO_3)_2$,

[This supposition may be utelised in the case of other metals]

Equation of 1st step of the reaction is written as

$XCu^0+YH\overset{+5}{N}O_3 \rightarrow X\overset{+2}{Cu}O+Y\overset{+2}{N}O+H_2O$.

$X=5-2=3$; $Y=2-0=2$

Or, $3Cu+2HNO_3 \rightarrow 3CuO+2NO+H_2O$...(1)

*F*inal step of the equation :

Reacting with $6HNO_3$ molecules, 3 CuO molecules produce $3Cu(NO_3)_2$ molecules.

$\therefore$ $3CuO+6HNO_3 \rightarrow 3\,Cu(NO_3)_2+3H_2O$ ...(ii)

$\because$ 6H atoms produce $3H_2O$ molecules.

Adding equation (i) and (ii) we can write,

$$3Cu+8HNO_3^-=Cu(NO_3)_2+2NO+4H_2O.$$

Whether the equation is balanced, checked by the number of oxygen atoms in the both sides of the equation. The number is 24 in each side.

Ion-electron method :

In this method the main reaction is separated into two parts. Each part is called half reaction. Oxidation occurs in the 1st part and reduction in the *2nd*. In the half reaction both H^+ and OH^- must not be used. If the reaction is acidic, H^+ may be used. OH^- may be utelised when the reaction occurs in alkaline medium. Make equal number of electrons in each "half reaction" by simple multiplication of a number with each of the constituent of the reaction. Finally the two half reactions are added, the same substance (substances) is eliminated. As a result we get the balanced equation.

Examples :

1. When a zinc rod is immersed in copper sulphate solution, metallic copper is precipitated and zinc goes into solution.

Half reaction (oxidation) : $Zn^\circ-2e \rightleftharpoons Zn^{++}$

Half reaction (reduction) : $Cu^{++}+2e \rightleftharpoons Cu^\circ$

Total reaction : $Cu^{++}+Zn=Cu+Zn^{++}$

2. Potassium permanganate oxidises ferrous sulphate in dilute sulphuric acid solution.

Half reaction (oxidation) : $Fe^{++}-e \rightleftharpoons Fe^{+++}$ ... (i)

Half reaction (reduction) : $MnO_4^-+8H^++5e$
$\rightleftharpoons Mn^{++}+4H_2O$ .... (ii)

Multiplying equation (i) by 5 and adding the equation with the equation (ii) we get, $MnO_4^-+8H^++5Fe^{++}$
$=Mn^{++}+5Fe^{+++}+4H_2O.$

3. Zinc dust and caustic soda solution reduce a nitrate to ammonia.

Half reaction (oxidation) :

$$Zn+4OH^{-}-2e \rightleftharpoons ZnO_2^{--}+2H_2O \quad \cdots \quad (i)$$

Half reaction (reduction) :

$$NO_3^{-}+6H_2O+8e \rightleftharpoons NH_3+9OH^{-} \quad \cdots \quad (ii)$$

Multiply 4 with eqn (i) and add this eqn with eq (ii). As a result we get, $NO_3^{-}+4Zn+7OH^{-}=NH_3+4ZnO_2^{--}+2H_2O$, the balanced equation of the total reaction.

4. Zinc dissolves in sodium hydroxide solution to form hydrogen and sodium zincate.

Half reaction (oxidation) : $Zn+4OH^{-}-2e \rightleftharpoons ZnO_2^{--}+2H_2O$

Half reaction (reducton) : $2H_2O+2e \rightleftharpoons 2OH^{-}+H_2$

Total reaction : $Zn+2OH^{-}=\downarrow ZnO_2^{--}+\uparrow H_2$

5. Ammonium nitrite, on heating decomposes into nitrogen and water.

Half reaction (oxidation) : $2NH_4^{+}-6e \rightleftharpoons N_2+8H^{+} \quad \cdots \quad (i)$

Half reaction (reduction) :

$$NO_2^{-}+4H^{+}+3e \rightleftharpoons \tfrac{1}{2}N_2+2H_2O \quad \cdots \quad (ii)\times 2$$

Total reaction : $2NH_4^{+}+2NO_2^{-}=2N_2+2H_2O$

i. e., $2NH_4NO_2=2N_2+2H_2O$.

6. Hydrogen peroxide liberates iodine from acidified potassium iodide solution.

Half reaction (oxidation) : $2I^{-}-2e \rightleftharpoons I_2$

Half reaction (reduction) : $H_2O_2+2H^{+}+2e \rightleftharpoons 2H_2O$

Total reaction : $H_2O_2+2I^{-}+2H^{+}=2H_2O+I_2$

7. Potassium dichromate oxidises potassium iodide in dilute sulphuric acid medium.

Half reaction (oxidation) : $2I^{-}-2e \rightleftharpoons I_2 \quad \cdots \quad (i)\times 3$

Half reaction (reduction) :

$$Cr_2O_7^{--}+14H^{+}+6e \rightleftharpoons 2Cr^{+++}+7H_2O \quad \cdots \quad (ii)$$

Total reaction : $Cr_2O_7^{--}+14H^{+}+6I^{-}=2Cr^{+++}+7H_2O+3I_2$

8. When manganese dioxide is heated with concentrated hydrochloric acid, chlorine gas is evolved.

Half reaction (oxidation) : $2Cl^- - 2e \rightleftharpoons Cl_2$ ··· (i)

Half reaction (reduction) :

$$\underline{MnO_2+4H^++2e\rightleftharpoons Mn^{++}+2H_2O} \quad \cdots \quad (ii)$$

Total reaction : $MnO_2+4H^++2Cl^-=Mn^{++}+Cl_2+2H_2O$

or, $MnO_2+4H^++2Cl^-+2Cl^-=Mn^{++}+2Cl^-+Cl_2+2H_2O$

[$2Cl^-$ is added in both sides of the equation]

or, $MnO_2+4HCl=MnCl_2+Cl_2+2H_2O$.

Problems for practice :

1. Calculate the oxidation number of N in (a) HNO_3 (b) NH_3 and (c) NH_4Cl. Ans. +5, −3, −3.

2. Calculate the oxidation number of Mn in (a) MnO_2 ; (b) MnO ; (c) Mn_2O_7. U. *P*. 1977. Ans. +4, +2, +7, +7.

3. Calculate the oxidation number of S in (a) SO_4^{--} ; (b) SO_2 ; (c) SO_3 and (d) H_2SO_3. Ans. +6, +4, +6, +4.

4. Calculate the oxidation number of C in (a) CO_3^{--} ; (b) CO and (c) calcium carbonate. Ans. +4, +2, +4.

5. Calculate the oxidation number of C in (a) CCl_4 ; (b) C_2H_5OH ; (c) $CHCl_3$ and (d) $C_2H_4I_2$.

Ans. +4, −2, +2 and −1.

6. Calculate the change in the value of oxidation number of (a) nitrogen when (i) NO is oxidised into NO_2 (ii) HNO_3 is reduced to NH_3 ; (b) chlorine when hydrogen chloride is oxidised into chlorine and (c) sulphur when hydrogen sulphide is oxidised to sulphuric acid. Ans. (a) 2 magnitude increase, 8 magnitude decrease ; (b) 1 magnitude increase and (c) 8 magnitude increase.

7. Complete and balance the following chemical equations by either oxidation number method or ion-electron method :

(i) $S+HNO_3=\cdots$ (ii) $MnO_2+HCl=\cdots$ (iii) $KBr+H_2SO_4 \rightarrow K_2SO_4+Br_2+SO_2+H_2O$ (W. *B. J. E. E. 1979*)

(iv) $KMnO_4+HCl\rightarrow KCl+MnCl_2+Cl_2+H_2O$ (*W. B. J. E. E.* 1979)

(v) $FeCl_2+Cl_2=\cdots$

8. How are the oxidation and reduction processes involved in the following reactions : *Ranchi. U. 1970A.*

(i) $2FeCl_2 + Cl_2 = 2FeCl_3$;

(ii) $C + 4HNO_3 = CO_2 + 2H_2O + 4NO_2$.

9. Write down with the help of equations, how you have reduced (a) mercuric chloride, (b) potassium permanganate, (c) copper sulphate and (d) lead nitrate soln. Balance the equations either by ion-electron method or oxidation number method. *Patna University.*

10. Balance the equations of the following reactions either by oxidation number method or ion-electron method :

(a) HNO_3 oxidises C into CO_2, itself being reduced to NO_2, the other product is H_2O ; (b)HNO_3 oxidises H_2S to S ; NO and H_2O are also produced in the reaction and (c) $KMnO_4$ is reduced by H_2O_2 in dil H_2SO_4 medium. *Hyderabad. I. Sc. 1974.*

11. Complete and balance the following equations :

(a) $P_4 + I_2 + H_2O = H_3PO_4 + \cdots\cdots$ *I.I.T. 1970 (gp.A)*

(b) $HNO_2 = HNO_3 + NO + \cdots\cdots$ *I.I.T.* 1971 *(gp.A)*

(c) $NH_3 + NaOCl = N_2 + NaCl + \cdots\cdots + H_2O$

I. I. T. 1971 *(gp. A)*

(d) $Br_2 + OH^- = BrO^- + \cdots\cdots + H_2O$ *I. I. T.* 1974 *(gp. A)*

(e) $Cr_2O_7^{--} + SO_2 + H = \cdots + HSO_4^- + H_2O$,,

(f) $NH_4NO_2 \overset{\Delta}{=} \cdots\cdots + \cdots\cdots$,,

12. Balance the following reactions by oxidation number method : (i) $KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + Fe_2(SO_4)_3 + H_2O$; (ii) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$. *U. P.* 1978. ; *West Bengal Joint Entrance Examination.* 1978. '79.

13. (a) Balance the following equations :

(i) $MnO_2 + HCl = H_2O + MnCl_2 + Cl_2$.

Hyderabad I. Sc. 1973 ; *W. B. J. E. E.* 1980.

(ii) $CO + Fe_3O_4 = FeO + CO_2$.

(iii) $PI_3 + H_2O = H_3PO_3 + HI$.

(iv) $Cl_2 + IO_3^- + OH^- = IO_4^- + Cl^- + H_2O$.

(v) $HNO_3 + HI = NO + I_2 + H_2O$.

(vi) $HgS+HCl+HNO_3=H_2HgCl_4+NO+S+H_2O$.

(vii) $C+H_2SO_4\rightarrow CO_2+SO_2+H_2O$.

W. B. J. E. E. (Tc). 1979.

(b) Complete, if necessary and balance the following equations :

(i) $Cr_2O_7^{2-}+HNO_2+H^+=$ .... $+NO_3^-+H_2O$.

(ii) $Ag+NO_3^-+H^+=Ag^++$ ··· $+H_2O$.

(iii) $H_2O_2+ClO_2+OH^-=$ ··· $+O_2+H_2O$.

I. I. T. (Group A) 1978.

14. Balance the following equations : *Hyderabad* I. *Sc.* 1973.

(a) $Cl_2+I^-\rightarrow I+Cl^-$; (b) $ClO_4^-+Sn^{++}\rightarrow Cl+Sn^{++++}$.

15. Balance the equation ; $Mn_3O_4+H_2SO_4\rightarrow MnSO_4+Mn_2(SO_4)_3+H_2O$. *Hyderabad I. Sc.* 1974.

16. Consider the following reaction : $Cl_2+2I^-=2Cl^-+I_2$. State which one of the reactants is the oxidising agent and which one is the reducing agent, giving reasons in electronic terms. *W. B.* J. E. E. *1979.*

17. Find the oxidation number of all the former elements in the following :—(i) $S_2O_3^{2-}$ (ii) BaO_2 (iii) LiH (iv) $C_2O_4^{2-}$ (v) N_2H_4. Ans. +2, +4, +1, +3 & +2.

I. I. T. (Group A) 1978.

18. Calculate the oxidation numbers of Mn in K_2MnO_4 or MnO_4^{--} and Cl in $KClO_3$. U. *P. 1977S* ; *W. B. H. S. C. 1979.*

Ans. +6 and +5.

19. Give the oxidation number (with sign) of the element underlined in the following equations :

(i) $8K\underline{Cl}O_3+24HCl=8KCl+12H_2O+9\underline{Cl}_2+6\underline{Cl}O_2$

(ii) $3\underline{I}_2+6NaOH=Na\underline{I}O_3+5Na\underline{I}+3H_2O$.

I. I. T. 1979. Ans. +5, 0, +4, 0, +5, −1.

20. Determine the oxidation numbur of pt in $[PtCl_6]^{--}$ and of P in PO_4^{-3}. U. *P. 1977* ; *'77S.* Ans. +4 ; +5.

21. Choose either the oxidant and reductant or oxidising and reducing agent in the following reactions :

(i) $2I'+H_2O_2\rightarrow 2OH^-+I_2$ *Roorkee E. E. 1976.*

(ii) $SnCl_2+2HgCl_2 \rightarrow SnCl_4+Hg_2Cl_2$ U. *P. 1978S.*

(iii) $PbS+4H_2O_2 \rightarrow PbSO_4+4H_2O$ U. *P. 1976.*

(iv) $4HCl+MnO_2 \rightarrow MnCl_2+2H_2O+Cl_2$ U. *P. 1978.*

(v) $SnCl_2+FeCl_3 \rightarrow SnCl_4+FeCl_2$ U. *P. 1977.*

(vi) $2FeCl_3+H_2S \rightarrow 2FeCl_2+2HCl+S$ U. *P. 1977S.*

22. Explain with reasons which one of the following reactions is oxidation which one is reduction :

$Zn-2e^- \rightarrow Zn^{2+}$; $Cl_2+2e^- \rightarrow 2Cl^-$ U. *P. 1976.*

23. On the basis of change in the oxidation number find out the oxidising and reducing agents in the following equation. U. *P. 1978S.*
$SnCl_2+2HgCl_2 \rightarrow SnCl_4+Hg_2Cl_2$.

24. Find the oxidation number of the marked atom in the following compounds: (i) $\underline{Fe_3}O_4$ (ii) $O\underline{F_2}$ (iii) $\underline{K}O_2$ (iv) $K_2\underline{Cr_2}O_7$ and (v) $\underline{Cr_2}O_7''$. Ans. +2·6 ; +1 ; +4, +6 & +6.

25. (a) Calculate the oxidation number of Mn in $KMnO_4$, K_2MnO_4 and MnO. (b) Which of the following indicates oxidation ? (i) $Sn^{+4} \rightarrow Sn^{+2}$; (ii) $Cl^{\circ} \rightarrow Cl^-$; (iii) $Fe^{+2} \rightarrow Fe^{+3}$; (iv) $Pb^0 \rightarrow Pb^{+2}$. *Ravisankar* U. (*M. P.*) *B. Sc. 1978.*

Ans. (a) +7 ; +6 & +2. (b) (iii) & (iv).

26. Balance the equation using oxidation number method :
$FeCl_3+H_2S \rightarrow FeCl_2+HCl+S$. *W. B.* J. *E. E. 1980.*

27. Complete and balance the following equations :

(i) $KNO_3+FeSO_4+H_2SO_4$ (conc) =

(ii) $H_2S+K_2CrO_4+H_2SO_4=$

(iii) $KI+H_2SO_4$ (conc.) [heat] =

(iv) $Mg_3N_2+H_2O=$

(v) $Al+KMnO_4+H_2SO_4=$ *I. I. T. 1980.*

28. State, with equations, what happens when—

(a) $NaNO_2$ soln is added to a solution of KI acidified with H_2SO_4 excess ; (b) Na_2CO_3 solution is added to a solution of $FeCl_3$; (c) SO_2 gas is passed through a suspension of iodine in water ; (d) H_2S gas is passed through a solution of potassium dichromate acidified with dil. H_2SO_4 ; (e) a pinch of MnO_2 is added to hydrogen peroxide solution. *W. B.* J. *E. E. 1980.*

29. Complete the following equations, with the help of 'oxidation number' :—

(i) $H_2S + SO_2 \rightarrow S + H_2O$ (ii) $FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$.

W. B. H. S. C. 1980.

4 unit decrease

[Hints : (i) $\overset{+2-2}{H_2S} + \overset{+4-4}{SO_2} \longrightarrow S^\circ + S^\circ + \overset{+2-2}{H_2O}$.

2 unit increase

$$4H_2S + 2SO_2 \longrightarrow 6S + 4H_2O$$

or, $2H_2S + SO_2 \longrightarrow 3S + 2H_2O$

4 unit decrease

(ii) $\overset{+4-4}{FeS_2} + O_2^\circ \longrightarrow \overset{+6\ \ -6}{Fe_2\ \ O_3} + \overset{+4-4}{SO_2}$

2 unit increase

$$4FeS_2 + \underset{+9O_2}{2O_2} \longrightarrow 2Fe_2O_3 + 8SO_2.$$

or, $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$.

CHAPTER 15

Structural formulae of some organic compounds with correct naming according to I. U. P. A. C. or I. U. C (Geneva) system.

A committee, appointed by the International Union of chemists of pure and applied chemistry held meeting in Geneva and adopted a new convention for naming of different classes of organic compounds. This convention is known as I. U. P. A. C or commonly I. U. C or Geneva system. As this convention, adopted in the meeting of renouned chemists of the world, held in Geneva, the convention is called Geneva system of nomenclature.

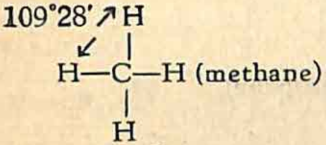
Some rules of the I. U. P. A. C (Geneva) system :

(1) I. U. P. A. C system does not make use of the prefixes, like normal (*n*−), iso−and neo−to distinguish various isomeric forms (compounds having same molecular formula but having

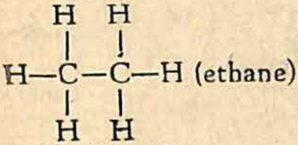
different structural formulae, named isomers) of alkanes. (2) The carbon atoms in the longest chain are numbered from one end to the other and the positions of side-chains or substituents are indicated by the numbers of the carbon atoms to which they are attached in the alkanes. The end from which numbering, commenced in is so chosen that the various substituents must get the positions of the lowest numbers of carbon atoms. (3) If there are more than one side chains or substituents, they should be arranged in an alphabetical order.

Examples :

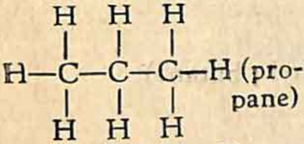
Aliphatic saturated hydrocarbon (Parafins or alkanes)



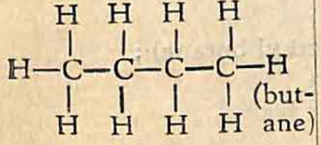
$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}H}$ (methane)



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$ (ethane)



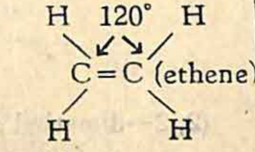
$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$ (propane)



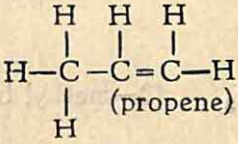
$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$ (butane)

Aliphatic unsaturated hydrocarbon

Alkenes



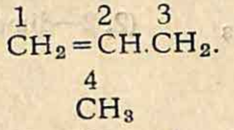
(ethene)



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}{-}H}$ (propene)

For butene

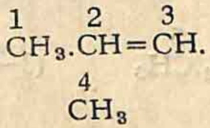
either,



$\overset{1}{\mathrm{CH_2}}=\overset{2}{\mathrm{CH}}.\underset{\overset{4}{\mathrm{CH_3}}}{\overset{3}{\mathrm{CH_2}}}.$

(but—1—ene)

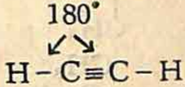
or,



$\overset{1}{\mathrm{CH_3}}.\overset{2}{\mathrm{CH}}=\underset{\overset{4}{\mathrm{CH_3}}}{\overset{3}{\mathrm{CH}}}.$

(but—2—ene or isobutene)

Alkynes



$\mathrm{H{-}C{\equiv}C{-}H}$ (ethyne)

$\mathrm{CH_3.C{\equiv}CH}$ (propyne)

For butyne

either,

$\overset{4}{\mathrm{CH_3}}.\overset{3}{\mathrm{CH_2}}.\overset{2}{\mathrm{C}}{\equiv}\overset{1}{\mathrm{CH}}$

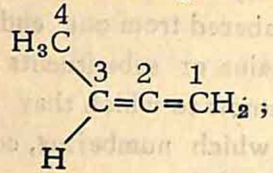
But—1—yne

or,

$\overset{4}{\mathrm{CH_3}}.\overset{3}{\mathrm{C}}{\equiv}\overset{2}{\mathrm{C}}.\overset{1}{\mathrm{CH_3}}$

But—2—yne

Alkene having two double bonds

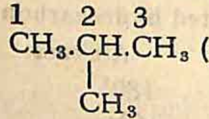


$\overset{4}{CH_2}=\overset{3}{CH}.\overset{2}{CH}=\overset{1}{CH_2}$

1, 2—butadiene 1, 3—butadiene

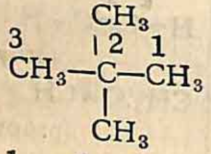
N.B. "ene" is a symbol for double bond between two carbon atoms. "yne" stands for triple bond between two carbon atoms. The combination of di and ene is to indicate two double bonds. "·" stands for single bond.

Alkyl group substituted alkanes



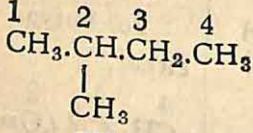
$\overset{1}{CH_3}.\underset{CH_3}{\overset{2}{CH}}.\overset{3}{CH_3}$

(2—methyl propane) ;



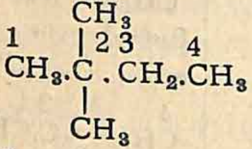
$\overset{3}{CH_3}-\underset{CH_3}{\overset{\overset{CH_3}{2}}{C}}-\overset{1}{CH_3}$

(2, 2—dimethyl ; propane)



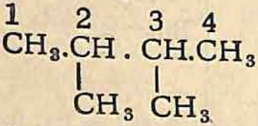
$\overset{1}{CH_3}.\underset{CH_3}{\overset{2}{CH}}.\overset{3}{CH_2}.\overset{4}{CH_3}$

(2—methyl butane) ;



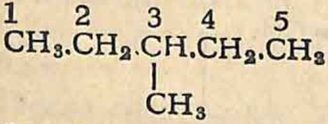
$\overset{1}{CH_3}.\underset{CH_3}{\overset{\overset{CH_3}{2}}{C}}.\overset{3}{CH_2}.\overset{4}{CH_3}$

(2, 2—dimethyl ; butane)



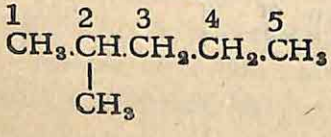
$\overset{1}{CH_3}.\underset{CH_3}{\overset{2}{CH}}.\underset{CH_3}{\overset{3}{CH}}.\overset{4}{CH_3}$

(2, 3—dimethyl butane) ;



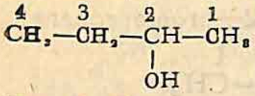
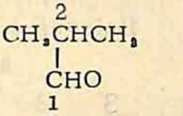
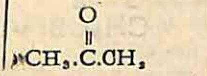
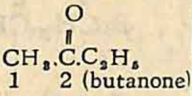
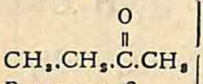
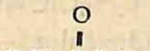
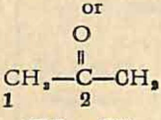
$\overset{1}{CH_3}.\overset{2}{CH_2}.\underset{CH_3}{\overset{3}{CH}}.\overset{4}{CH_2}.\overset{5}{CH_3}$

(3—methyl pentane) ;



$\overset{1}{CH_3}.\underset{CH_3}{\overset{2}{CH}}.\overset{3}{CH_2}.\overset{4}{CH_2}.\overset{5}{CH_3}$

(2—methyl pentane)

Aliphatic alcohols	*Aliphatic aldehydes and ketones* *Aldehydes*	*Aliphatic acids*	*Ethers*
$CH_3.OH$ (methanol) 2 1 $CH_3.CH_2.OH$ (ethane—1—ol) 3 2 1 $CH_3.CH_2.CH_2OH$ (propane—1—ol or 1—propanol) 3 2 1 $CH_3.C.H.OH.CH_3$ (propane—2—ol or 2—propanol) 4 3 2 $CH_2—CH_2—CH_2$ 1 $—CH_2—OH$ (But—1—ol)  $\overset{4}{CH_3}—\overset{3}{CH_2}—\underset{OH}{\overset{2}{CH}}—\overset{1}{CH_3}$ (But—2—ol) $(CH_3)_3C.OH$ (t—butanol)	HCHO (methanal) 1 $CH_3.CHO$ 2 1 (ethanal) $CH_3.CH_2.CHO$ 3 2 1 (propanal)  $CH_3\underset{\underset{1}{CHO}}{\overset{2}{CH}}CH_3$ (2—methyl propanalor butanal *Ketones*  $CH_3.\overset{O}{\overset{\|}{C}}.CH_3$ (propanone)  $\underset{1}{CH_3}.\underset{2}{\overset{O}{\overset{\|}{C}}}.C_2H_5$ (butanone) or,  $CH_3.CH_2.\overset{O}{\overset{\|}{C}}.CH_3$ Butanone—2  $C_2H_5.\overset{O}{\overset{\|}{C}}.C_2H_5$ (pentanone) or  $\underset{1}{CH_3}—\underset{2}{\overset{O}{\overset{\|}{C}}}—CH_3$ $—CH_2—CH_3$ 2—pentanone or pentane—2—on.	HCOOH (methanoic acid) 2 1 CH_3COOH (ethanoic acid) 3 2 1 $CH_3.CH_2.COOH$ (propanoic acid) C_3H_7COOH (butanoic acid) or 4 3 2 $CH_3.CH_2.CH_2$ 1 COOH (1—propane carboxylic acid)	$CH_3—O—CH_3$ (methoxy methane $CH_3—O—C_2H_5$ (methoxy ethane) $C_2H_5—O—C_2H_5$ (ethoxy ethane)

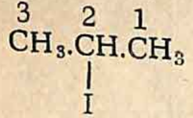
N. B. In the I. U. P. A. C (Geneva) syytem an aldehyde is named by replacing "al" in place of 'ane" of hydrocarbon. The carbon atom in the aldehyde is considered as 1 position carbon. "ol" and "on" stand for alcohol and ketone respectively. An organic monobasic or mono carboxylic acid is named by replacing "oic" in place of "ane" of hydrocarbon. The carbon atom in the monocarboxylic acid is considered as 1 position carbon. When one of the hydrogen atoms of methane (CH_4) is replaced by methoxy group (CH_3O—), it is called methoxy methane. When one of the hydrogen atoms of ethane (C_2H_6) is replaced by ethoxy group (C_2H_5O—), it is called ethoxy ethane.

Halogen substituted alkanes

$\overset{1}{CH_3Cl}$ (1—chloromethane)

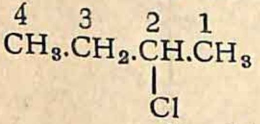
$\overset{2}{CH_3}.\overset{1}{CH_2Cl}$
(1—chloroethane)

$\overset{3}{CH_3}.\overset{2}{CH_2}.\overset{1}{CH_2Cl}$
(1—chloroproane)

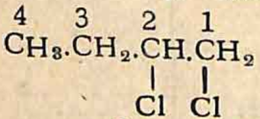

$\overset{3}{CH_3}.\underset{\substack{|\\ I}}{\overset{2}{CH}}.\overset{1}{CH_3}$

(2—iodo propane)

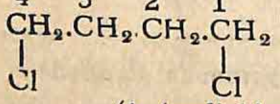
$\overset{4}{CH_3}.\overset{3}{CH_2}.\overset{2}{CH_2}.\overset{1}{CH_2Cl}$
(1—chlorobutane)


$\overset{4}{CH_3}.\overset{3}{CH_2}.\underset{\substack{|\\ Cl}}{\overset{2}{CH}}.\overset{1}{CH_3}$

(2—chlorobutane)


$\overset{4}{CH_3}.\overset{3}{CH_2}.\underset{\substack{|\\ Cl}}{\overset{2}{CH}}.\underset{\substack{|\\ Cl}}{\overset{1}{CH_2}}$

(1, 2—dichlorobutane)


$\underset{\substack{|\\ Cl}}{\overset{4}{CH_2}}.\overset{3}{CH_2}.\overset{2}{CH_2}.\underset{\substack{|\\ Cl}}{\overset{1}{CH_2}}$

(1, 4—dichlorobutane)

Halogen substituted alkenes and alkynes

$\overset{3}{CH_3}.\overset{2}{CH}=\overset{1}{CHBr}$
(1—bromopropene)

$\overset{3}{CH_3}\overset{2}{CBr}=\overset{1}{CH_2}$
(2—bromopropene)

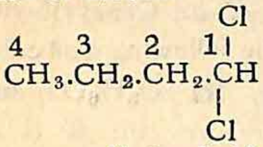
$\overset{3}{BrCH_2}.\overset{2}{CH}=\overset{1}{CH_2}$
(3—bromopropene)

$\overset{3}{CH_3}.\overset{2}{C}\equiv\overset{1}{CBr}$
(1—bromopropyne)

$\overset{3}{CH_2Cl}\overset{2}{C}\equiv\overset{1}{CCl}$
(3—chloro—1—chloropropyne)

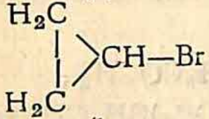
Halogen substituted alkanes

N. B. In the I. U. P. A. C (Geneva) system, position of halogen is known by the position of carbon.



$$\overset{4}{C}H_3.\overset{3}{C}H_2.\overset{2}{C}H_2.\overset{1}{C}HCl_2$$

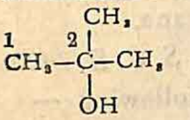
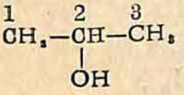
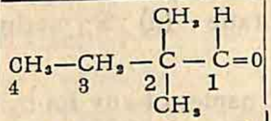
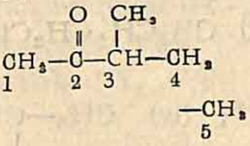
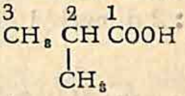
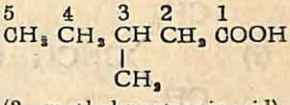
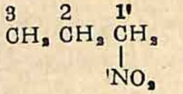
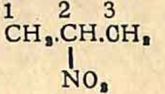
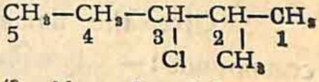
(1, 1—dichlorobutane)



(bromo cyclopropane)

Cyclo stands for ring structure.

Halogen substituted alkenes and alkynes

Alkyl group substituted alcohol	*Alkyl group substituted aldehyde and ketone*	*Alkyl group substituted acids*
 $\overset{1}{C}H_3-\overset{2}{C}(CH_3)(OH)-CH_3$ (2—methyl propane—2—ol)  $\overset{1}{C}H_3-\overset{2}{C}H(OH)-\overset{3}{C}H_3$ (Propane—2—ol) $(CH_3)_2\overset{2}{C}H.\overset{1}{C}H_2OH$ [2—methyl propane—1—ol)	 $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}(CH_3)_2-\overset{1}{C}H=O$ (2, 2—dimethyl butanal)  $\overset{1}{C}H_3-\overset{2}{C}O-\overset{3}{C}H(CH_3)-\overset{4}{C}H_2-\overset{5}{C}H_3$ (3—methyl—2—pentanone) or (3—methylpentane—2—on)	 $\overset{3}{C}H_3\,\overset{2}{C}H(CH_3)\,\overset{1}{C}OOH$ (2—methyl propanoic acid)  $\overset{5}{C}H_3\,\overset{4}{C}H_2\,\overset{3}{C}H(CH_3)\,\overset{2}{C}H_2\,\overset{1}{C}OOH$ (3—methyl pentanoic acid)
Amino (—NH_2) *group substituted organic compound* $C_2H_5NH_2$ (aminoethane)	*Nitro group* (—NO_2) *substituted organic compounds*  $\overset{3}{C}H_3\,\overset{2}{C}H_2\,\overset{1}{C}H_2NO_2$ (1—nitropropane)  $\overset{1}{C}H_3.\overset{2}{C}H(NO_2).\overset{3}{C}H_3$ (2—nitropropane)	*Two different groups substituted organic compounds*  $\underset{5}{C}H_3-\underset{4}{C}H_2-\underset{3}{C}H(Cl)-\underset{2}{C}H(CH_3)-\underset{1}{C}H_3$ (3—chloro—2 methyl pentane) $\underset{3}{C}H_3\,\underset{2}{C}H(NH_2)\,\underset{1}{C}OOH$ 2—amino propanoic acid.

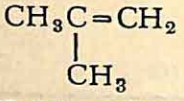
Questions for practice :

1. What is I. U. P. A. C system ? Explain with illustrations how this system is used in the nomenclature of organic compounds.

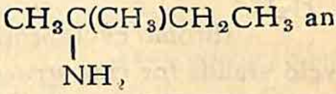
2. Write down the names (I. U. P. A. C or Geneva) with structures of the compounds having the following molecular formulae : (a) C_4H_{10}, (b) C_3H_8O ; (c) C_3H_6O and (d) C_4H_8.

3. Give the names of the following organic compounds by I. U. P. A. C system :

(i) $CH_3\,CH_2\,CH\,(CH_3)\,CH_3$; (ii) CH_3COCH_3 ;

(iii) 

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$;

(iv) 

$CH_3\underset{\displaystyle NH_2}{\underset{|}{C}}(CH_3)CH_2CH_3$ and

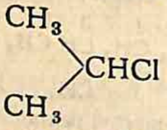
(v) $C.CH_3\equiv CH$. *Sambalpur U. I. Sc. 1978.*

4. Write the structural formulae for the following :—

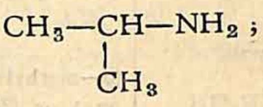
(i) 2 : 2 dimethyl butane ; (ii) 3 – methyl pentane.

I. S. C. E. 1980.

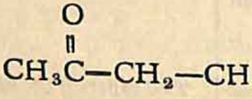
5. Give the IUPAC names of any four of the following :—

(i) 

$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CHCl$; (ii) $CH_3CH_2CH_2Cl$;

(iii) $CH_3CH_2CH_2OH$; (iv) 

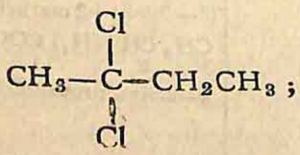
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$;

(v) 

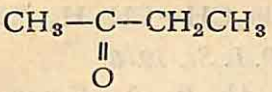
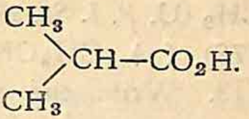
$CH_3\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_3$; and (vi) $C_2H_5-O-C_2H_5$.

I. S. C. E. 1980.

6. Give the names (Geneva) of the following organic compounds :—

(i) 

$CH_3-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-CH_2CH_3$; (ii) $CH_3CH=CHCH_3$;

(iii) 
$CH_3-\underset{\overset{\|}{O}}{C}-CH_2CH_3$ and (iv) 

W. *B. H. S. C. 1978.*

7. Give the structural formulae of the following organic compounds :—

(i) 2—methyl propanoic acid ; (ii) 2—methyl butane ; (iii) 2—nitro—2—methyl butane ; (iv) 2—methyl 1—propene ; (v) 2—2 diiodo butane ; (vi) benzene and (vii) benzyne.

8. Give I. U. P. A. C. names of the following compounds :—

(i) $CH_3.O.CH_3$; (ii) $CH_3.CH_2.CH_2.OH$ and (iii) the next homologue of CH_3COOH.

Indian School Certificate Examination, 1978.

9. Write the structural formula of the following compounds :—

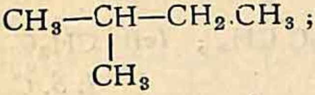
(i) 2—methyl pentane &

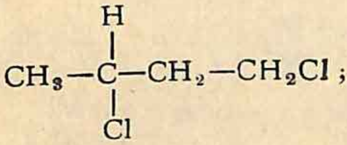
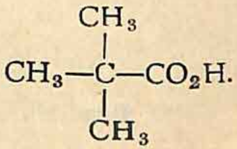
(ii) 2—ethyl—3—methyl—Butene—1.

Indian School Certificate Examination, 1978.

10. (a) Write the structural formulae and names of all the compounds having the molecular formula $C_4H_{10}O$.

(b) Give the names (Geneva) of the following :

(i) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2.CH_3$; (ii) $CH_3-CH_2-CH=CH_2$;

(iii) 
$CH_3-\underset{Cl}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_2-CH_2Cl$; (iv) 
$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CO_2H$.

W. B. H. S. C. 1979.

11. The angle between the two adjacent carbon—carbon bonds in the benzene molecule is 120°. Is this statement correct ? State giving reasons. *W. B. H. S. C. 1979.*

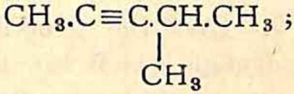
12. Give the I. U. P. A. C. names of the following :—

(i) $CH_3CH_2CH_2OH$ (U. *P. I. Sc.* 1976.) (ii) CH_3CH_2CH

$=CH_2$ (U. *P. I. Sc.* 1977) (iii) $CH_3CH=CHCH_3$ (U. *P. I. Sc.* 1977*S*) (iv) $CH_3CHClCH_3$ (U. *P. I. Sc. 1978*)

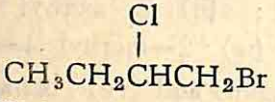
13. Write the systematic I. U. P. A. C names of the following :—

(i) $CH_3.CH=CH.CH_2OH$; (ii)



$CH_3.C\equiv C.\underset{\substack{|\\CH_3}}{CH}.CH_3$;

(iii)



$CH_3CH_2\overset{\substack{Cl\\|}}{C}HCH_2Br$; (iv) $CH_3.CH_2.CH_2.CO.CH_2Cl$.

(b) Write the structural formulae of (i) phenol (ii) 2, 4 dimethyl pentanoic acid (iii) 1, 3—butadiene (iv) 2—methyl pentane 2—ol—1.

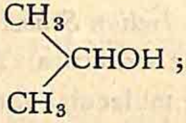
Ravisankar U. *B. Sc.* 1974.

14. Write the graphic formulae of any four :—(a) Diethyl ether ; (b) Isopropyl alcohol ; (c) Chloroform ; (d) 2, 2, 4 trimethyl pentane ; (e) 3 ethyl—2 methyl pentane.

Ravisankar U. *B. Sc. 1973.*

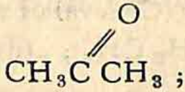
15. Give the IUPAC names of any four of the following :—

(i) CH_3CH_2OH ; (ii)

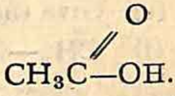


$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH$; (iii) CH_3CHO ;

(iv) $CH_3OC_2H_5$; (v)



$CH_3\overset{\overset{O}{\|}}{C}CH_3$; (vi)



$CH_3\overset{\overset{O}{\|}}{C}-OH$.

I. S. C. E. 1979.

CHAPTER 16

Problems on Kinetic theory of gases

Kinetic gas equation

$PV=\frac{1}{3}mnv^2$. Where, P=pressure, V=volume, m=mass of single molecule and v=root mean square velocity, (R. M. S. V.). With the aid of the 'kinetic theory of gasess', it is possible to derive mathematically the above mentioned equation. The equation is known as kinetic gas equation.

Specific heats of gases.

$C_p=M\times c_p$ & $Cv=M\times cv$. Where C_p and Cv are molar heats or molecular specific heats at constant pressure and at constant volume. M represents molecular weight of a gas. c_p and cv are specific heats per gm at constant pressure and volume.

$C_p=\frac{5}{2}R+X$, $Cv=\frac{3}{2}R+X$, X is intramolecular energy.

R=universal molar gas constant. $C_p-Cv=R$ for 1 gm mole ideal gas. $M(c_p-cv)=R$; $c_p-cv=\frac{R}{M}$ for 1 gm ideal gas.

$X=0$, for monatomic gas i.e. atomicity=1.
$X=R$, for diatomic " " " 2.
$X=\frac{3}{2}R$, for polyatomic " " " >2.

Atomicity represents number of atoms constituting the molecule.

$$\frac{C_p}{Cv}=\frac{\frac{5}{2}R+X}{\frac{3}{2}R+X} \qquad \because \frac{C_p}{Cv}=\frac{M\times c_p}{M\times cv}=\frac{c_p}{cv}=\gamma.$$

$$\therefore \gamma=\frac{\frac{5}{2}R+X}{\frac{3}{2}R+X}.$$ Where, γ is called specific heats' ratio.

Limiting density

At low pressure, $M=\left(\frac{d}{p}\right)_0 RT$. $\left(\frac{d}{p}\right)_0$ is known as limiting density.

$$\underset{p\to 0}{\mathrm{Lt}}\left(\frac{d}{p}\right)=\left(\frac{d}{p}\right)_0.$$ Where, d=density of the gas ; p=pressure.

Van der Waals' equation of state

$\left(P+\frac{a}{V^2}\right)(V-b)=RT$ for 1 gm mole real gas.

a, b are constants, known as Van der Waals' constants.

$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$ for n gm. mole real gas.

$\left(P+\frac{aw^2}{V^2M^2}\right)\left(V+\frac{w}{M}b\right)=\frac{w}{M}RT$ for „ „ „ “

$n=\frac{w}{M}$. w = weight in gms of a real gas ; M = molecular weight of the gas.

$\frac{RT_c}{P_cV_c}=\frac{8}{3}=2{\cdot}66$. This ratio is called critical co-efficient or "Kammerling—Onnes" constant. Value of this constant is calculated from Van der Waals' equation of state at the critical state. P_c, V_c & T_c are critical pressure, critical volume and critical temperature respectively.

$V_c=3b$, $P_c=\frac{a}{27b^2}$ and $T_c=\frac{8a}{27bR}$.

Root mean square velocity (R. M. S. V)

Total translational kinetic energy = sum of translational kinetic energy of all molecules.

$\frac{1}{2}mNC^2=\frac{1}{2}mn_1c_1{}^2+\frac{1}{2}mn_2c_2{}^2+\frac{1}{2}mn_3c_3{}^2+\ldots\ldots$

c = velocity possessed by each molecule.

m = mass of each molecule.

or, $Nc^2=n_1c_1{}^2+n_2c_2{}^2+n_3c_3{}^2+\cdots\cdots n_ic_i{}^2$.

or, $\overline{c^2}=\frac{n_1c_1{}^2+n_2c_2{}^2+n_3c_3{}^2+\ldots\ldots n_ic_i{}^2}{N}$

$\therefore$ R. M. S. $V=\sqrt{\overline{c^2}}=\sqrt{\frac{n_1c_1{}^2+n_2c_2{}^2+\cdots\cdots+n_ic_i{}^2}{N}}$.

$\overline{c^2}$ = mean square velocity of each molecule.

$$\text{R. M. S. V}=\sqrt{\frac{3RT}{M}}.$$

Average translational kinetic energy.

Average translational kinetic energy/mole $= \frac{3}{2}RT$.

„ „ „ „ /molecule $= \frac{3R}{2N}T$.

N = avogadro's number

Solved problems :

1. The density of hydrogen at 0°C and 760 mm pressure is 0·00009 gm ml^{-1}. Find the root mean square velocity of hydrogen molecules. (density of mercury = 13·6 gm. ml^{-1})

Behrampur University. 1970.

$PV = \frac{1}{3}mnv^2$ or, $P = \frac{1}{3}\rho.v^2$ $\because$ $\rho = \frac{mn}{V} =$ density.

$$v = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 981}{0{\cdot}00009}} = 1{\cdot}15 \times 10 \text{ cms/sec at } 0°C.$$

$\rho = h \times d \times g$. Where, h = height of Hg ; d = density of Hg and g = acceleration due to gravity.

2. What is the density of CO_2 at 127°C if confined under a pressure of 2280 mm of Hg.

$P = \frac{1}{3}\rho.v_s^2$ or, $\rho = \frac{3P}{v_s^2}$

$$= \frac{3 \times 228 \times 981 \times 13{\cdot}6}{\frac{3RT}{M}} \quad \because \quad v^2 = \frac{3RT}{M}.$$

$$\rho = \frac{3 \times 228 \times 981 \times 13{\cdot}6 \times M}{3RT} = \frac{228 \times 981 \times 13{\cdot}6 \times 44}{8{\cdot}31 \times 10^7 \times 400}$$

$= 0{\cdot}00403$ gm cc^{-1}. $\because$ $R = 8{\cdot}31 \times 10^7$ ergs ; $M = 44$.

3. Calculate the total kinetic energy in calories of 1 gm of CO_2 gas at 27°C. *Calcutta University B. Sc. 1974.*

1 gm $CO_2 = \frac{1}{44}$ gm mole CO_2. $\because$ mol. wt of $CO_2 = 44$.

$\therefore$ total kinetic energy $= \frac{1}{44} \times \frac{3}{2} \times 1{\cdot}987(273+27) = 20{\cdot}32$ cals.

$\because$ K. E $= \frac{3}{2}nRT$. Here, $n = \frac{1}{44}$; $R = 1{\cdot}987$ cal/deg/mole.

4. The specific heat of chlorine at constant volume is 0·082 and at constant pressure, 0·115. One litre of the gas at N. T. P. weighs 3·151 gms. Calculate the approximate at. wt of chlorine.

22·4 litres of chlorine at N. T. P. weigh $3{\cdot}151 \times 22{\cdot}4 = 70{\cdot}58$ gms.

$\therefore$ mol. wt of chlorine $= 70{\cdot}58$. $\gamma = \frac{c_p}{cv} = \frac{0{\cdot}115}{0{\cdot}082} = 1{\cdot}40$.

Chlorine is therefore diatomic and its at. wt $= \frac{70{\cdot}58}{2} = 35{\cdot}29$.

5. The specific heat of a gas at constant pressure is 0·125 and that at constant volume is 0·075. What is the mol. wt of the gas?

Calcutta U. *B. Sc.* (*A*) *1973* ; *Guru Nanak* U. *B. Sc. 1974.*

$c_p - cv = \frac{R}{M}$ or, $M = \frac{R}{c_p - cv} = \frac{2}{0{\cdot}125 - 0{\cdot}075} = 40$.

6. The specific heat at constant volume for argon is 0·075 and its molecular weight is 40. How many atoms are there in the molecule? *Gauhati.* U. *B. Sc. 1968.*

$Mcv = \frac{3}{2}R + X$ or, $40 \times 0{\cdot}075 = \frac{3}{2} \times 2 + X$ $\therefore$ $X = 0$.

There is only single atom in the molecule of argon.

7. Calculate the amount of heat required to raise the temperature of 20 gms of He from 20°C to 100°C (i) at constant pressure, and (ii) at constant volume. ($R = 1{\cdot}99$ cal. deg^{-1}. mole^{-1} ; at. wt of He = 4) *Calcutta* U. *B. Sc. 1975.*

(i) $H_p = C_p = \frac{5}{2}RT$ for 1 gm mole $\because$ He is monatomic.

$X = 0$. $H_p = C_p = \frac{5}{2} \times 2 \times 80 \times \frac{20}{4} = 1990$ cals.

(ii) $Uv = Cv = \frac{3}{2} \times 2 \times 80 \times \frac{20}{4} = 1194$ cals.

Where, U = internal energy, H = enthalpy.

8. The limiting density of hydrogen bromide is 3·611 at 0°C. Calculate the exact at. wt of bromine.

$$M = \left[\frac{d}{p}\right]_0 = 3{\cdot}611 \times 0{\cdot}0821 \times 273 = 80{\cdot}924.$$

$\because$ $\left[\frac{d}{p}\right]_0 = 3{\cdot}611$. At. wt of hydrogen $= 1{\cdot}008$

$\therefore$ at wt of bromine $= 80{\cdot}924 - 1{\cdot}008 = 79{\cdot}916$.

9. Apply Vander Waals' equation to calculate the pressure exerted by 70 gm nitrogen contained in a half litre vessel at 27°C. [Given $a = 1{\cdot}29$ atm. litre^2. mole^{-2} ; $b = 0{\cdot}039$ litre mole^{-1}]

Burdwan U. (*W. B.*) *B. Sc. 1968.*

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

or $$\left(P+\frac{2.5\times2.5\times1.29}{0.5\times0.5}\right)(0.5-2.5\times0.039)$$

$$=2.5\times0.0821\times300$$

$\because$ $n=\frac{70}{28}$; R $=0.0821$ lit. atm/deg/mole.

$\therefore$ $P=118.045$ atms.

10. Show that at low pressure, the Van der Waals' equation reduces to the form $PV=RT+\left(b-\frac{a}{RT}\right)P$.

Delhi. U. B. Sc. 1970.

$\left(P+\frac{a}{V^2}\right)(V-b)=RT$ for 1 gm mole real gas.

or, $PV-Pb+\frac{a}{V}-\frac{ab}{V^2}=RT$ on multiplication.

At low pressure $\frac{ab}{V^2}$ may be ignored, then

$PV=RT+Pb-\frac{a}{V}$. or, $PV=RT+Pb-\frac{aP}{RT}$

$\because$ $PV=RT$ is valid at low pressure.

or, $PV=RT+P\left(b-\frac{a}{RT}\right)$

11. The Van der Waals' constants for nitrogen gas are $a=1.39$ atm. lit^2. mole^{-2}, and $b=3.91\times10^{-2}$ lit. mole^{-1}. Find the values of the critical constants for the gas. (R $=0.08206$ lit. atm. deg^{-1}. mole^{-1}) *Calcutta* U. *B. Sc. 1974.*

$V_c=3b=3\times3.91\times10^{-2}=11.73\times10^{-2}$ lit. mole^{-1}.

$$P_c=\frac{a}{27b^2}=\frac{1.39}{27\times11.73\times11.73\times10^{-4}}=33.67 \text{ atms.}$$

$$T_c=\frac{8a}{27bR}=\frac{8\times1.39}{27\times11.73\times10^{-2}\times0.08206}=128.3^\circ A$$

Problems for Practice :

1. Calculate the root mean square speed of helium molecules at 27°C. Also calculate the total kinetic energy (in cals) of the molecules in one litre of helium at 27°C and 1 atm.

Calcutta U. *B. Sc. 1971.*

[He = 4] Ans. $13{\cdot}6\times10^{4}$ cms/sec ; 36·55 cals.

2. Calculate the root mean square speed of nitrogen at N. T. P. *Patna* U. *1969A.* Ans. 49330 cms/sec.

3. Calculate the average kinetic energy of helium molecules at 27°C. *Burdwan* U. *B. Sc. 1968.* Ans. $6{\cdot}2\times10^{-4}$ ergs.

4. Calculate the root mean square speed and the average kinetic energy of oxygen molecules at 27°C. *Burdwan* U. *B. Sc. 1970.* Ans. 273,000 cms/sec ; $6{\cdot}209\times10^{-18}$ ergs/molecule.

5. Calculate the R. M. S velocity of hydrogen molecule at N. T. P. *Rajasthan* U. *B. Sc. 1971* ; *Shivaji* U. *1971.*

Ans. 20·7 cms/sec.

6. Calculate the root mean square velocity in centimetres per sec of N_2 molecules at 27°C and 127°C ($R = 8{\cdot}315\times10^{7}$ erg deg^{-1} $mole^{-1}$). *Sri Venkateswara 1971* ; *Calcutta* U. *B. Sc. 1971* ; *Sambalpur* U. *1974.* Ans. $5{\cdot}169\times10^{4}$ cms/sec ; $5{\cdot}968\times10^{4}$ cms/sec.

7. Calculate (i) the root mean square velocity and (ii) the average kinetic energy per mole of oxygen at 27°C. (Given : $R = 8{\cdot}315\times10^{7}$ erg deg^{-1} $mole^{-1}$) *Calcutta* U. *B. Sc. 1977.*

Ans. $4{\cdot}84\times10^{3}$ cms/sec ; $3{\cdot}742\times10^{10}$ ergs.

8. At what temperature will the root-mean-square velocity of nitrogen molecule be $5{\cdot}16\times10^{4}$ cms/sec ? ($R = 8{\cdot}31\times10^{7}$ ergs/deg/mole) *Calcutta* U. *B. Sc. 1978.* Ans. 26°C.

9. Calculate the root mean square speed of a molecule of oxygen at 127°C. *Calcutta* U. *B. Sc. (A) 1979.*

Ans. $5{\cdot}582\times10^{4}$ cms/sec.

10. A gas has 1·4 as the value of Cp/Cv. If its atomic weight is *X*, what will be its molecular weight ? *Poona* U. *1970.*

Ans, 2X.

11. How much heat will be required to raise the temperature of 10 gms of Argon from 0°C to 100°C at a pressure of 1 atm ? ($R = 1{\cdot}99$ cal deg^{-1} $mole^{-1}$; atomic weight of Argon = 39·95). *Calcutta* U. *1971*. Ans 124·6 cals.

12. For a certain gas, $T_c = 304{\cdot}2$°K and $P_c = 72{\cdot}8$ atm. Hence calculate Vander Waals' constants '*a*' and 'b' for the gas. *Calcutta* U. *B. Sc. 1973.* Ans. $a = 0{\cdot}036 \times 10^2$ atm. lit^2. $mole^{-2}$; $b = 4{\cdot}28 \times 10^{-2}$ lit. $mole^{-1}$.

13. Using Van der Waals equation, calculate the pressure exerted by one mole of carbon dioxide at zero degree centrigrade in a volume of 0·05 litre. $a = 3{\cdot}592$ lit^2. atm. $mole^{-2}$ and $b = 0{\cdot}04267$ lit. $mole^{-1}$. *Poona* U. *B. Sc. 1970.* Ans. 1622 atms.

14. Using the Van der Waals' equation calculate the pressure (in atmospheres) developed by 2 moles of CO_2 contained in a volume of 5 litres at 40°C. (The values of the Van der Waals' constants for CO_2 are : $a = 3{\cdot}59$ lit^2 atm. $mole^{-2}$, $b = 0{\cdot}0427$ lit. $mole^{-1}$. Also, $R = 0{\cdot}0821$ lit. atm. $mole^{-1}$.) *Calcutta* U. *1972.*

Ans. 9·8655 atm

15. Use the equation of state of Van der Waals to calculate the pressure of 88 gms of gaseous carbon dioxide occupying a volume of 8 litres at 27°C ($a = 3{\cdot}6$ lit^2. atm. $mole^{-2}$; $b = 0{\cdot}043$ lit. $mole^{-1}$, $R = 0{\cdot}082$ lit. atm. deg^{-1}. $mole^{-1}$). Compare the above result with the pressure calculated using ideal gas equation. *Shivaji* U. *1970.* Ans. 5·993 atms ; 6·15 atms.

16. Use Van der Waals' equation to calculate the temperature at which 1 mole of N_2 will occupy a volume of 5 litres at a pressure of 15 atms (Van der Waals' constants for N_2 : $a = 1{\cdot}39$ lit. atm. $mole^{-1}$; $b = 0{\cdot}0391$ litre. $mole^{-1}$; also $R = 0{\cdot}08206$ lit. atm. deg^{-1}, $mole^{-1}$) and compare the result with that calculated using the ideal gas equation. *Calcutta* U. *B. Sc. 1975.*

Ans. 910·5°K or, 637·5°C ; 914·1°K or, 641·1°C.

17. One mole of carbon dioxide was found to occupy a volume of 1·32 litres at 48°C at a pressure of 18·40 atm. Calculate the pressure that would have been expected (i) from ideal

gas behaviour (ii) from Van der Waals' equation. [$a=3{\cdot}60$ litre^2. atm. mole^{-2} and $b=4{\cdot}28\times10^{-2}$ litre. mole^{-1}]. *Sambalpur* U. *B. Sc. 1973.* Ans. (i) 19·96 atms ; (ii) 18·575 atms.

18. Using Van der Waals' equation, calculate the pressure (in atms) developed by 2 moles of N_2 contained in a volume of 5 litres at 40°C (Van der Waals' constants for N_2 are $a=1{\cdot}38$ lit^2. atm. mole^{-2}, $b=0{\cdot}0394$ lit. mole^{-1}. Also, $R=0{\cdot}0821$ lit. atm. mole^{-1}). *Calcutta* U. *B. Sc. 1974.* Ans. 25·94 atms.

19. Calculate the pressure of 2 moles of ammonia when confined in a five litre vessel at 27°C from (i) the ideal gas equation and (ii) Van der Waals' equation. (Given $a=4$ atm. lit^2/mole^2 ; $b=0{\cdot}036$ lit/mole). *Calcutta University B. Sc. 1979.*

Ans. 9·84 atms ; 9·34 atms.

20. Calculate the velocity, as used in the kinetic equation, of oxygen molecule at 15°C and 770 mm pressure. *Calcutta* U. *B. Sc. 1980.* Ans. 47390 cms/sec.

21. The kinetic energy of a molecule of oxygen at 0°C is $5{\cdot}62\times10^{-14}$ ergs. Calculate the value of Avogadro's number. ($R=8{\cdot}316\times10^7$ ergs. deg^{-1} mole^{-1}). *Calcutta* U. *B. Sc.* (*New*). *1980.* Ans. $6{\cdot}023\times10^{23}$.

CHAPTER 17

Problems on Thermodynamics (Energetics)

Theory :—**Work in reversible isothermal process**

The gas will not expand unless the pressure of the surroundings is less than that of the gas. Maximum work is obtained when the pressure of the surroundings is only infinitesimally less than the pressure of the gas at all times during the expansion from volume V_1 to V_2. Substituting P gas for P surr, in the equation, $W=\int_{V_1}^{V_2} P \text{ surr } dV$, we can write $W \max=\int_{V_1}^{V_2} P \text{ gas } dV$ and if the gas is assumed to be ideal the substitution of $P=\frac{nRT}{V}$

may be done. $W_{\max}=nRT\int_{V_1}^{V_2}\frac{dV}{V}=nRT\ \text{In}\ \frac{V_2}{V_1}=nRT\ \text{In}\ \frac{P_1}{P_2}$

$=nRT\ 2{\cdot}303\log\frac{P_1}{P_2}\quad\because\quad P_1V_1=P_2V_2$ for isothermal expansion of an ideal gas.

The work for isothermal reversible expansion of one mole of a Van der Waals' gas (real gas) is given by the equation,

$$W=\int_{V_1}^{V_2}PdV=\int_{V_1}^{V_2}\left(\frac{RT}{V-b}-\frac{a}{V^2}\right)dV$$

$\left[\because\ \left(P+\frac{a}{V^2}\right)(V-b)=RT\right.$ for 1 gm mole real gas (Van der Waals equation.)]

$$W=RT\ \text{In}\frac{V_2-b}{V_1-b}+a\left[\frac{1}{V_2}-\frac{1}{V_1}\right]$$

$$=RT\ 2{\cdot}303\log\frac{V_2-b}{V_1-b}+a\left[\frac{1}{V_2}-\frac{1}{V_1}\right].$$

For n gm moles,

$$W=nRT\ \text{In}\frac{V_2-nb}{V_1-nb}+an^2\left[\frac{1}{V_2}-\frac{1}{V_1}\right]$$

$$=nRT\ 2{\cdot}303\log\frac{V_2-nb}{V_1-nb}+an^2\left[\frac{1}{V_2}-\frac{1}{V_1}\right].$$

Adiabatic process : For adiabatic change,

(a) $P_1V_1^{\gamma}=P_2V_2^{\gamma}=\text{constant}.$

Where, $\gamma=\frac{C_p}{C_v}=$ specific heats' ratio ;

$C_p=\frac{dH}{dT}$; $C_v=\frac{dU}{dT}$. $dH=$ enthalpy.

(b) $T_1V_1^{\gamma-1}=T_2V_2^{\gamma-1}=\text{constant}.$

(c) $T_1P_1^{\frac{1-\gamma}{\gamma}}=T_2P_2^{\frac{1-\gamma}{\gamma}}=\text{constant}.$

$\triangle W=\frac{1}{1-\gamma}\left[P_2V_2-P_1V_1\right]=\frac{1}{1-\gamma}\left[RT_2-RT_1\right]$ for 1 gm mole ideal gas.

Work in irreversible isothermal process :

During irreversible expansion pressure P_1 rapidly changes from P_1 to P_2 and the gas expands isothermally at the pressure P_2. Work done is given by $W_{ir} = P_2(V_2 - V_1)$ for 1 gm mole ideal gas.

Convention : $\Delta W = +ve =$ work done by the system ;

$\Delta W = -ve =$ work done on the system i.e., work done by the surroundings ; $\Delta Q = +ve =$ heat absorbed by the system ;

$\Delta Q = -ve =$ heat left from the system.

Efficiency of an engine

$$\eta = \text{efficiency} = \frac{\text{Work produced}}{\text{Heat supplied}} = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2}.$$

$\eta = 1 - \frac{Q_1}{Q_2}$. Engine takes up Q_2 cals heat from the source, a portion of it is utelised in performing work (W) and the rest (Q_1 cals) returns back to the sink. $W = Q_2 - Q_1$.

$$\text{Again, } \eta = \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2} = \frac{Q_2 \Delta T}{T_2}.$$

$\because$ $\Delta T = T_2 - T_1$. $T_2 =$ temperature of the source ; $T_1 =$ temperature of the sink. $T_2 > T_1$.

$$\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2} \quad \therefore \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}.$$

$\frac{W_{max}}{Q_2}$ is known as thermodynamic efficiency of the process.

Entropy : $ds = \frac{dQ_{rev}}{T}$; $ds =$ change in entropy ; dQ_{rev} = reversible heat change of the system. $T =$ temperature.

From 1*st* law of Thermodynamics,

$dQrev = dU + dW = Pdv$ $\because$ $dU =$ change in internal energy $= 0$ for ideal gas at constant temperature. $\int dQrev = \int Pdv$

$$\text{or,} \quad \Delta Qrev = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}.$$

$$\Delta S = S_B - S_A = \int_{S_A}^{S_B} d\ S = \int \frac{dQrev}{T} = \frac{nRT}{T} \ln \frac{V_2}{V_1} = nR \ \ln \ \frac{V_2}{V_1}$$

$$= nR\ 2{\cdot}303\ \log \frac{V_2}{V_1} = nR\ 2{\cdot}303\ \log \frac{P_1}{P_2}.$$

$\Delta S = \frac{Qrev}{T} = \frac{mL}{T}$. Where, m = mass of the liquid vaporised ; L = latent heat of vaporisation at constant T.

$$\Delta S = S_B - S_A = \int_A^B dS = \int_{T_1}^{T_2} \frac{dQrev}{T} = \int_{T_1}^{T_2} \frac{msdT}{T}$$

or, $\Delta S = ms \int_{T_1}^{T_2} d\ \ln T = ms\ \ln \frac{T_2}{T_1} = ms\ 2{\cdot}303\ \log \frac{T_2}{T_1}$.

Where, s = specific heat of the liquid ; ΔS = entropy change.

$\Delta H = \Delta U + \Delta(PV)$. Where ΔH = change in heat content = enthalpy.

At the constant pressure, $\Delta H_p = \Delta U + P\Delta V$

$\because$ $\Delta P = 0$ or, $\Delta H_p = \Delta Q_p$ from 1st law of thermodynamics.

Entropy change from ice to steam

Total change of entropy $= \frac{L_1}{T_i} + 2{\cdot}303 \log \frac{T_s}{T_i} + \frac{L_2}{T_s}$

L_1 = latent heat of ice ; T_i = temperature during conversion of ice into water ; T_s = temperature of steam ; L_2 = latent heat of steam.

Joule-Thomson expression

$\mu = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$ for 1 gm mole Van der Waals' gas.

$\mu = \frac{1}{C_p}\left(\frac{2na}{RT} - nb\right)$ for n gm mole gas.

μ = Joule-Thomson coefficient ; Cp = Molar specific heat at constant pressure ; a, b = Vander Waals' constants.

Solved Problems

1. What is the maximum work obtained when 600 gms of mercury vapour are allowed to expand at 500°C from 6 atm to 3 atm pressure. Given molecular weight of Hg vapour 200.

Calcutta University B. Sc.

Mercury vapour is assumed to behave ideally.

We have, $W \max = \frac{600}{200} \times 2 \times (273+500) \times 2{\cdot}303 \log\frac{6}{3}$.

$= 3215$ cals.

$\because$ $W \max = \frac{W}{M}$ RT $2{\cdot}303 \log\frac{P_1}{P_2}$ & $R = 2$ cals.

2. Calculate the amount of heat absorbed in cals when ten gramme molecules of a perfect gas expand reversibly at 27°C from 100 litres to 1000 litres. *Calcutta University B. Sc.*

$\Delta W = nRT \ln\frac{V_2}{V_1} = nRT\ 2{\cdot}303 \log\frac{V_2}{V_1} = 10 \times 2 \times 300$

$\times 2{\cdot}303 \log\frac{1000}{100} = 13818$ cals. $\because$ $\Delta U = 0$ for a perfect gas at constant temperature.

$\therefore$ $\Delta Q = \Delta W$ from 1*st* law of thermodynamics. Hence, $\Delta Q = 13818$ cals = amount of heat absorbed.

3. The volume of one mole of an ideal monatomic gas initially at 2 atmospheres and 25°C is doubled by reversible adiabatic expansion. Calculate the final pressure and temperature.

Calcutta University B. Sc.

We have, $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$; $V_2 = 2V_1$;
$\gamma = 1{\cdot}66$; $T_1 = 298°A$; $T_2 = ?$ $298(V_1)^{1\cdot66-1} = T_2(2V_1)^{1\cdot66-1}$

$\therefore$ $T_2 = 188{\cdot}9°A$. Again, $P_1V_1^{\gamma} = P_2V_2^{\gamma}$ or, $2(V_1)^{1\cdot66} = P_2(2V_1)^{1\cdot66}$ $\therefore$ $P_2 = 0{\cdot}63$ atm.

4. Calculate the workdone in the adiabatic and reversible expansion of 2 litres of a perfect monatomic gas from 5 to 1 atm, the final volume being 2·74 litres. *Calcutta University B. Sc.*

$\Delta W = \frac{1}{1-\gamma}[P_2V_2 - P_1V_1] = \frac{1}{1-1{\cdot}66}[2{\cdot}74 - 5 \times 2]$
$\gamma = 1{\cdot}66$, $\therefore$ $\Delta W = 11$ litre. atm.

5. Five moles of argon (assumed ideal) expand isothermally from 10 litres to 25 litres at 40°C. Calculate the workdone (in lit. atm) when the expansion takes place (i) reversibly, and (ii) against a constant external pressure of 1 atm. ($R=0{\cdot}08206$ lit. atm. deg^{-1} $mole^{-1}$). *Calcutta University B. Sc. 1975.*

(i) $\Delta W=nRT\ 2{\cdot}303\log\frac{V_2}{V_1}=5\times0{\cdot}08206\times(273+40)$

$\log\frac{25}{10}=117{\cdot}7$ lit. atm.

(ii) $W_{ir}=P_2(V_2-V_1)=1(25-10)=15$ lit. atm.

6. One mole of Van der waals' gas expands isothermally reversibly from 2 litres to 20 litres at 27°C. Calculate the work done if $a=1{\cdot}42\times10^{12}$ dynes cm^4 per mole and $b=30$ cc per mole. Given, $R=8{\cdot}31\times10^7$ ergs/deg/mole.

$$\Delta W=RT\ 2{\cdot}303\log\frac{V_2-b}{V_1-b}+a\left[\frac{1}{V_2}-\frac{1}{V_1}\right]$$

$$=2{\cdot}303\times8{\cdot}31\times10^7(273+27)\log\frac{20-0{\cdot}03}{2-0{\cdot}03}+1{\cdot}42\times10^{12}$$

$$\left[\frac{1}{20000}-\frac{1}{2000}\right]=56{\cdot}77\times10^9\text{ ergs.}$$

7. 70 gm nitrogen gas expands isothermally against a constant external pressure of 1 atm. It was initially at 50 atm at 25°C. Calculate work done assuming the gas to behave ideally.

$P_1=50$ atm ; $P_2=1$ atm ; $\Delta W=P_2(V_2-V_1)$

$=P_2\left(\frac{nRT}{P_2}-\frac{nRT}{P_1}\right)\ \because\ PV=nRT.$

$n=\frac{70}{28}=2{\cdot}5$ gm. moles. $R=2$ cals. Mol. wt of nitrogen $=28$.

$$\Delta W=\frac{nRTP_2(P_1-P_2)}{P_2P_1}=\frac{2{\cdot}5\times2\times298\times1(50-1)}{50\times1}=1500\text{ cals.}$$

8. Calculate the efficiency of a reversible engine working between the heat source and sink temperatures 500°C and 150°C respectively. *Calcutta University B. Sc. 1974.*

$\eta=1-\frac{T_1}{T_2}$. $T_1=273+150=423°A$; $T_2=773°A$.

$\eta=1-\frac{423}{773}=1-0{\cdot}547=0{\cdot}453$. % efficiency $=45{\cdot}3$.

9. A Carnot's engine is operated between two reservoirs at temperatures of 450°K and 350°K. If the engine receives 1000

calories of heat from the source, calculate the efficiency of the engine and the workdone by the engine.

$Q_2=1000$ cals ; $T_2=450^\circ K$; $Q_1=?$; $T_1=350^\circ K$.

$$\frac{Q_1}{Q_2}=\frac{T_1}{T_2} \text{ or, } Q_1=\frac{T_1}{T_2}\times Q_2=\frac{350}{450}\times 1000=777.77 \text{ cals.}$$

$$\eta=\frac{W}{Q_2}=\frac{Q_2-Q_1}{Q_2}=1-\frac{777.77}{1000}=0.2222.$$

% efficiency $=22.22$. $W=100-777.77=222.23$ cals.

10. An engine works between 600°K and 300°K being capable of having an efficiency of 52%. Elucidate the fact.

$$\eta=1-\frac{T_1}{T_2}=1-\frac{300}{600}=0.5. \text{ \% efficiency}=50.$$

The efficiency claimed is absurd because of the fact that the efficiency of the engine is more than the efficiency of a Carnot's engine working between the same two temperature limit. As no engine can have an efficiency more than a Carnot's engine, the efficiency claimed is not justified.

11. Calculate the change in entropy which occurs when 25 gm moles of a perfect gas expands reversibly and isothermally at 57°C, from 150 litres to 900 litres. *Calcutta University B.Sc.*

$$\Delta S=nR2.303 \log\frac{V_2}{V_1}=25\times 2\times 2.303 \ \log\frac{900}{150}$$

$\because R=2$ cals. $\therefore \Delta S=89.60$ cals.

12. Estimate the inversion temperature and the Joule—Thomson coefficient of oxygen at the standard state if its Van der Waals' constants are $a=1.36$ lit^2. atm. mole^{-2} and $b=0.0317$ lit. mole^{-1}. [$C_p=6.9$ cal mole^{-1}.deg^{-1}.]

$$Ti=\frac{2\times 1.36}{0.0317\times 0.0821}=1040^\circ A \ \because Ti=\frac{2a}{bR}=\text{inversion temperature.}$$

Now, μ = temperature coefficient

$$=\frac{1}{C_p}\left(\frac{2a}{RT}-b\right)=\frac{1}{\frac{6.9\times 0.0821}{2}}\left(\frac{2\times 1.36}{0.0821\times 273}-0.0317\right)$$

$=0.315^\circ A$ per atm. $\because R=2$ cals $=0.0821$ lit. atm & $T=273^\circ A$.

13. Calculate the minimum work that must be done at 25°C on 2 mole CO_2 to compress them from a volume of 20 liters to a volume of 1 litre, when CO_2 is assumed (a) to be a perfect gas ;

and (b) to follow Van der waals' equation. For CO_2, $a=3{\cdot}61$ atm. lit^2. $mole^{-2}$ and $b=0{\cdot}045$ $lit.mole^{-1}$.

$$\text{(a)}\quad \triangle w=-\int_{V_1}^{V_2} Pdv=-nRT\ 2{\cdot}303\log\frac{V_2}{V_1}$$

$$=-2\times 2\times 298\times 2{\cdot}303\log\tfrac{1}{20}$$

$$=2\times 2\times 298\times 2{\cdot}303\log 20=3553 \text{ cals.}$$

$$\text{(b)}\quad \Delta w=-\int_{V_1}^{V_2} Pdv=-\int_{V_2}^{V_2}\left(\frac{nRT}{V-nb}-\frac{an^2}{V^2}\right)dv$$

$$=nRT\ 2{\cdot}303\ \log\ \left(\frac{V_1-nb}{V_2-nb}\right)-an^2\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

$$=\left[2\times 0{\cdot}0821\times 298\times 2{\cdot}303\log\left(\frac{20-0{\cdot}09}{1-0{\cdot}09}\right)\right.$$

$$\left.-3{\cdot}61\times 2\times 2\left(\frac{20-1}{1\times 20}\right)\right]=3325 \text{ cals.}$$

14. 10 litre helium at N.T.P were heated in a vessel to 100°C. Calculate the change in energy and enthalpy.

$PV=nRT$ or $1\times 10=n\times 0{\cdot}0821\times 273$ or $n=\dfrac{10}{0{\cdot}0821\times 273}$

$=0{\cdot}446$. Now, $dU=nCvdT=n.\frac{3}{2}RdT=0{\cdot}446\times 3\times 100$

[∵ n = number of moles of helium $=0{\cdot}446$; $R=2$ cals ;

$dT=100$; $Cv=\frac{3}{2}R$ (vide. kinetic theory of gases).]

∴ $dU=133{\cdot}8$ cals. Change in energy $=133{\cdot}8$ cals. Change in enthalpy $=dH=nCpdT=0{\cdot}446\times\frac{5}{2}R\times 100=0{\cdot}446\frac{5}{2}\times 2\times 100$ $=223$ cals.

∴ change in enthalpy $=223$ cals. For helium intramolecular enegy factor $=0$. ∴ $Cv=\frac{3}{2}R$; $Cp=\frac{5}{2}R$.

15. One mole of steam is condensed reversibly at its boiling point 100°C and 1 atm.pressure. Calculate change in heat, workdone, energy, enthalpy and entropy.

Latent heat of steam $=540$ cals/gm. $R=2$ cals. deg^{-1}. $mole^{-1}$.

(a) Heat change $=\Delta Q=540\times 18=9720$ cals evolved = molar heat of condensation. (b) Δw = workdone, for water (vap) $\longrightarrow$ water (liq.). ∵ temperature is constant at boiling point

∴ workdone = $RT = 2 \times (100+273) = 746$ cals

∵ work is done on the vapours, ∴ $\Delta w = -746$ cals.

(c) $\Delta U = \Delta Q - \Delta w = 9720 + 746 = 10466$ cals = increase in internal energy. (d) ΔH = change in heat content = $\Delta U + \Delta(PV)$ $= \Delta U + P\Delta V$ ∵ $\Delta P = O$ for constant pressure ∴ ΔH_p $= \Delta U + P\Delta V$ or $\Delta Hp = \Delta Qp = 9720$ cals. (e) ΔS = change in entropy $= \frac{\Delta Q rev}{T} = -\frac{9720}{373} = -26{\cdot}058$ cal. deg^{-1} = decrease in entropy.

Problems for Practice

1. Calculate the maximum workdone in ergs for isothermal and thermodynamically reversible expansion of 5 moles of an ideal gas from a pressure of 2 atms to 10 atms at 25°C.

$(R = 8{\cdot}314 \times 10^7 \text{ ergs}^{-1} \text{ mole}^{-1})$

Mysore B.Sc. 1971. Ans. $-19932{\cdot}344 \times 10^7$ ergs. —ve sign indicates workdone on the system.

2. Three moles of a perfect gas expand isothermally and reversibly from 6·72 litres to 67·2 litres at 0°C. Calculate the workdone in calories and litre atmospheres. *Calcutta University B. Sc.* 1970. Ans. 3772·314 cals ; 154·853 lit. atm.

3. Two moles of N_2 at 25°C are expanded from 5 litres to 10 litres. Assuming the gas to be ideal, calculate the workdone (in lit. atm), when the expansion takes place (i) isothermally and reversibly, and (ii) against a constant external pressure of 1atm. $R = 0{\cdot}082$ (lit. atm. $mole^{-1}$). *Calcutta University* 1972. *B.Sc.* Ans. 33·878 lit. atm. ; 5 lit. atm.

4. A quantity of an ideal gas (Cv = 5 cals/deg/mole) at 25°C is allowed to expand adiabatically and reversibly from 200 atms. to 20 atms. Calculate final temperature (R = 2 cals/deg/mole). *Calcutta University B. Sc. 1978.* Ans. $-118{\cdot}6$°C. [Hint. $Cp - Cv = 2$; $Cp/Cv = \gamma$]

5. 7 gms of nitrogen gas at 1 atm. pressure and at 27°C are compressd isothermally and reversibly till the volume is reduced to half its original volume. Calculate the workdone on the gas. *Calcutta University. B.Sc.* 1979. Ans. 4·263 lit. atm ; 104 cals.

6. Two moles of an ideal gas at 100°C are reversibly expanded to twice its volume. Calculate : (i) the workdone if the expansion takes place isothermally ; (ii) the change in temperature (indicate rise or fall) if the expansion takes place adiabatically. (Given : $R=0·0821$ lit. atm. mole^{-1} deg^{-1} ; $Cp/Cv = \gamma = 1·41$). *Calcutta University. B.Sc.* 1977 Ans. 42·45 lit. atm ; 92·3° (fall).

7. One mole of Van der waals' gas at 27°C expands isothermally and reversibly from 10 litres to 20 litres. Calculate the workdone. Given : $a=5·49$ lit^2 atm. mole^{-2} ; $b=0·064$ litre. mole^{-1}. Ans. 16·86 lit. atm.

8. What should be the temperature of the sink for efficiency to be unity ? *Punjabi B.Sc.* Ans.—273°C.

9. A Carnot's engine whose low temperature reservoir is at 7°C has an efficiency of 40%. It is desired to increase the efficiency to 50%. By how many degrees should the temperature of the source be increased ? Ans. 93·34°.

10. Two moles of hydrogen at standard conditions are compressed adiabatically and reversibly to a volume of 10 litres. Calculate the value of final pressure. (γ for $H_2=1·41$). *Calcutta U. B. Sc. 1980 (New).*

[Hints : $P_1V_1=2RT_1$; $V_1=\dfrac{2RT_1}{1·41P_1}=\dfrac{2\times 0·0821\times 273}{1}$

$=44·83$ lits. $P_1V_1^{\gamma}=P_2V_2^{\gamma}$; $1(44·83)^{1·41}=P_2(10)^{1·41}$

$\therefore$ $P_2=8·32$ atms.]

11. Calculate the entropy change involved in the conversion of one mole of liquid water at 373°K to vapour at the same temperature. (Latent heat of vaporization, ΔHvap.$=2·257$ KJ/g) *I. S. C. E. 1980.*

[Hints : $\Delta S=\dfrac{2·257\times 18}{373}=10·89\times 10^{-2}$ KJ/gm. mole/°K.]

12. An engine working between 273°K and 373°K takes up 200 cals of heat from the high temperature. Calculate the workdone and efficiency. Ans. 53·62 ; 26·8%.

13. Calculate the change in entropy when one mole of helium isothermally expands from 10 litres to 100 litres at 27°C. *Calcutta University B.Sc.* Ans. 4·606 cals.

[Hint. Helium is assumed to behave ideally. Expansion is carried out reversibly]

14. Calculate the change in entropy, when 3 moles of an ideal gas are expanded from a volume of 20 litres to 86 litres at 288°A. Ans. 8·75.

15. The Van de waals' constants for CO_2 gas are $a=3{\cdot}59$ $lit^2. atm. mole^{-2}$ and $b=0{\cdot}043$ lit. $mole^{-1}$. Calculate the Joule Thomson coefficient of the gas at 273°A. What is the inversion temperature of this gas ? [$Cp=8{\cdot}97$ cal. $mole^{-1}. deg^{-1}$]

Ans. 0·7526°A peratm ; 1040°A.

16. Calculate the Joule—Thomson coeffcient for 0_2 at 273°A from the following data :

$a=1{\cdot}35\times10^6$ atm, $b=32$ cc & $Cp=7{\cdot}03$ cals/°A.

Ans. 0·31°A/atm. cm^2.

17. Calculate the temperature of inversion for H_2 if the critical temperature be 22°A. Ans.—124·5°C.

18. Calculate the change in energy and enthalpy if 20 litres of Argon at S.T.P. were heated in a vessel to 373°K.

Ans. 267·9 cals ; 446·5 cals.

19. One mole of benzene is condensed reversibly at its boiling point 80°C and 1 atm pressure. Calculate q, w, ΔE, ΔH & ΔS. The molar heat of vaporisation is 7350 caI. $mole^{-1}$.

[$R=2$ cal. $deg^{-1}. mole^{-1}$] *Bombay University B.Sc.* 1970.

Ans. 7350 cals ; −706 cals ; 8056 cals ; 7350 cals and −20·82 cal. deg^{-1}.

CHAPTER 18

Problems on Chemical Kinetics

Chemical Kinetics deals with the study of the rate (speed) of chemical reactions.

For the general reaction, $aA+bB \rightarrow gC+fD$, the rate$=k[A]^a[B]^b$; where, k is the rate constant or the specific reaction rate of the aforementioned reaction. '[ ]' stands for concentration. $(a+b)$ determines the *order of this reaction.* The *molecularity* is the total number of molecules of the reactants involved as indicated by the chemical equation balanced by least number of molecules.

For *a first order reaction* an equation of the following form can easily be derived, $t=\frac{2·303}{k_1}\log\frac{a}{a-x}$, where, a is the inital concentration of the reactant, $a-x$ is the concentration of the reactant, after a time t from the very beginning of the reaction, x is the used concentration and k_1 is the rate constant.

The time taken to change the concentration of a reactant to half its initial value is independent of the initial concentration of the reactant. This 'time' is called as *half life perjod* of a chemical reaction.

When $t=t_{\frac{1}{2}}$=half life period, then $x=\frac{a}{2}$. Putting the data in the expresson.

$t=\frac{2·303}{k_1}\log\frac{a}{a-x}$. We can write $t_{\frac{1}{2}}=\frac{2·303}{k_1}\log\frac{a}{a-\frac{a}{2}}=\frac{2·303}{k_1}\log 2$ $=\frac{0·693}{k_1}.\left(t_{\frac{1}{2}}\neq\frac{t}{2}\right)$

The *unit of rate constant* 'k_1' is determined as follows :—

$$k_1=\frac{2·303}{t}\log\frac{a}{a-x}=\frac{1}{[\text{time}]}\frac{[\text{moles/litre}]}{[\text{moles/litre}]}$$

$\because$ 2·303 is dimensionless. $\therefore$ $k_1=\frac{1}{\text{time}}=\text{time}^{-1}$.

Time can either be expressed in hour, minute or second, k_1

will then be expressed in $hour^{-1}$, $minute^{-1}$ or $second^{-1}$. Examples of first order reactions are the decomposition of nitrogen pentoxide to nitrogen tetroxide and oxygen, acid hydrolysis of ester, inversion of cane sugar etc.

For a second order reaction an equation of the following type can also be derived, $k_2 = \frac{1}{t} \frac{x}{a(a-x)}$, where a is the concentration of the reactant, $a-x$ is the concentration after a time t from the commencement of the reaction, x is the used concentration and k_2 is the rate constant.

$$\text{when } t = t_{\frac{1}{2}}\ ;\ x = \frac{a}{2} \quad \text{then} \quad t_{\frac{1}{2}} = \frac{1}{k_2} \cdot \frac{\frac{a}{2}}{a(a-\frac{a}{2})} = \frac{1}{k_2} \cdot \frac{1}{a}$$

The unit of rate constant 'k_2' is determined as follows :—

$$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)} = \frac{1}{\text{seconds}} \times \frac{\text{moles/litre}}{(\text{moles/litre})(\text{moles/litre})}$$

$$\text{or,} \quad k_2 = \frac{1}{\text{sec}} \cdot \frac{1}{\text{moles/litre}} = (\text{sec})^{-1} (\text{moles/litre})^{-1}.$$

The examples of the second order reactions are conversion of ozone into oxygen, thermal decomposition of nitrous oxide, saponification of esters etc.

Solved problems

1. Calculate (i) the specific rate constant, and (ii) the time required for 80% decomposition, for the thermal decomposition of gaseous acetone at 600°C (First order reaction with half life = 80 sec). *Calcutta* U. *B. Sc. 1977*.

$$k_1 = \frac{2{\cdot}303}{t} \log \frac{a}{a-x} \quad \text{and} \quad k_1 = \frac{0{\cdot}693}{t_{\frac{1}{2}}} = \frac{0{\cdot}693}{80} = 8{\cdot}662 \times 10^{-3}/\text{sec.}$$

$$\because \ t_{\frac{1}{2}} = 80 \text{ sec.} \quad \text{Now,} \ t = \frac{2{\cdot}303}{8{\cdot}662 \times 10^{-3}} \log \frac{a}{a - \frac{80}{100} a}$$

$$\text{or} \quad t = \frac{2{\cdot}303}{8{\cdot}662 \times 10^{-3}} \log \frac{1}{1-0{\cdot}8} = 185{\cdot}9 \text{ seconds.}$$

2. A solution containing equimolar amounts of sodium hydroxide and ethyl acetate is 25% saponified in 5 mins in a simple second order reaction. What would be $t_{\frac{1}{2}}$ of this reaction system? *Calcutta* U. *B. Sc. 1970.*

$$k_2=\frac{1}{t}\cdot\frac{x}{a(a-x)}=\frac{1}{5}\cdot\frac{\frac{25}{100}a}{a(a-\frac{25}{100}a)}=\frac{1}{15a}.$$

Now, $t_{\frac{1}{2}}=\frac{1}{k_2}\cdot\frac{1}{a}=\frac{1}{\frac{1}{15a}}\cdot\frac{1}{a}=15$ mins.

Problems for practice :

1. Time for half change in a mono molecular reaction is 25 minutes. What time will be required for 99·9% reaction ?
Poona U. *1970.* Ans. 249·15 mins.

2. The reaction $SO_2Cl_2=SO_2+Cl_2$ is a first order gas reaction with $k_1=2{\cdot}2\times10^{-5}\ \text{sec}^{-1}$ at 320°C. What percentage of SO_2Cl_2 is decomposed on heating this gas at 320°C for 90 minutes ? *Gauhati* U. *1970*. Ans. 11·2%.

3. The half time of certain first order reaction is 60 minutes. How long will it take for 90% of the reaction to occur ?
Bombay U. *1970.* Ans. 199·32 min.

4. The half life period of a first order reaction is 15 mins. Calculate the (i) rate constant, and (ii) time taken to complete 80% of the reaction. *Calcutta* U. *B.Sc. 1972.* Ans. 3·485 mins.

5. Calculate the time required for 90% completion of a first order reaction which is 50% complete in one hour.
Calcutta U. *B.Sc. 1975.* Ans. 3 hr. 19 min.

6. A gram mole of ethyl acetate was hydrolysed with a gm mole of NaOH when the concentration fell according to the following data. Show that the reaction is bimolecular and calculate the value of k.

t (min)	0	4	6	10	15	20
$a-x$	8·04	5·30	4·58	3·50	2·74	2·22

Udaipur 1970. Ans. 0·016/min or $1{\cdot}6\times10^{-2}$/min.

7. Show that the following data conforms to first order reaction. *Jiwaji 1971.*

Time in minutes (t)	0	10	20	30	40
conc of reactant (mole litre^{-1})	0·445	0·223	0·112	0·056	0·028.

8. A second order reaction is 20% completed in 500 seconds.

How long will it take for the reaction to go to 60% completion ? Ans. 50 minutes.

9. The first order rate constant for decomposition of N_2O_5 is $6{\cdot}2\times10^{-4}$ sec^{-1}. What is the half life period for this decomposition ? *Calcutta* U. *B.Sc. 1979.*

Ans. 1117·74 sec or 18 min 38 sec.

10. Where 75% of a reaction of the first order was completed in 32 mints, when was its half completed ? *Calcutta* U. *B. Sc.* (*New*). *1980.* Ans. 16 mints.

11. Calculate the age of a piece of hair in which C − 14 activity is 60% of the activity found to day. ($t_{\frac{1}{2}}$=5,760 yrs). *I. S. C. E. 1980.* Ans. $4{\cdot}256\times10^{3}$ yrs.

CHAPTER 19

Problems on conductance and transport number :

Theory : $R=\rho.\frac{l}{a}$ Where, R=resistance ; ρ=specific resistance ; l=distance between two plates of the cell having contained electrolytes' solution and a=area of the cross section of each plate of the cell. The reciprocal of resistance is called conductance or conductivity of the electrolyte's solution. The reciprocal of specific resistance is called specific conductivity i.e. $k=\frac{l}{e}$. Equivalent conductivity denoted by λ=specific conductance x volume containing one gm equivalent of electrolyte. i. e., $\lambda=k.\,V$. Where, k=specific conductance and V=volume containing one gm equivalent electrolyte. $\lambda=k.\frac{1000}{C}$; C=gm equivalent/litre. Cell constant$=\frac{l}{a}$=specific conductivity x observed resistance.

Degree of dissociation of electrolyte (α)

$$= \frac{\text{equivalent conductance at given dilution}}{\text{equivalent conductance at infinite dilution}} = \frac{\lambda v}{\lambda \alpha}.$$

From Kohlrausch's law of migration of ions,

$\lambda_{\alpha} = \lambda_{+} + \lambda_{-}$, where, λ_{+} = ionic conductance or ionic mobility due to cations and λ_{-} = ionic conductance or ionic mobility due to anions.

$\frac{\lambda_{+}}{\lambda_{-}} = \frac{t_{+}}{t_{-}} = \frac{\text{speed of cation}}{\text{speed of anion}} = \frac{u}{v}$. Where, t_{+} = transport number due to cation and t_{-} = transport number due to anion.

$$\lambda_{+} = t_{+}\lambda_{\alpha} \text{ and } \lambda_{-} = t_{-}\lambda_{\alpha}.$$

$$\text{Absolute ionic mobility} = \frac{\text{ionic conductivity}}{96500}$$

$$= \frac{\text{ionic conductance}}{F}.$$

For sparingly soluble salts, $\lambda_{\alpha} = \lambda_{+} + \lambda_{-} = k.\frac{1000}{C} = k.\frac{1000}{S}$.

Where, S = solubility.

Electrolysis with *attackable electrodes*, fall in concentration around cathode = increase in concentration around anode.

Electrolysis with *unattackable electrodes*, fall in concentration around cathode $\propto v$ and fall in concentration around anode $\propto u$.

$$t_{+} = \frac{u}{u+v}\,;\; t_{-} = \frac{v}{u+v}\,;\; \frac{t_{+}}{t_{-}} = \frac{u}{v} \text{ and } t_{+} + t_{-} = 1.$$

Transport number with *attackable electrodes*:

$t_{+} = \frac{w-(b-a)}{w}$. Where, w = weight of metal deposited in coulometer, a = concentration of anode solution before electrolysis and b = concentration of anode solution after electrolysis.

Transport number from moving boundary:

$t_{+} = \frac{V.C}{1000Q}$. Where, V = volume swept by the solution, C = concentration (gm. eq/litre) and Q = Faradays of electrcity passed during electrolysis.

$$Q=\frac{\text{current strength}\times\text{time}}{\text{Faraday}}=\frac{[\text{amp}][\text{sec}]}{9{,}6500}.$$

Solved Problems :

1. The resistance of a decinormal solution of a salt placed between two platinum electrodes 1·5 cm. apart and 5 sq. cm area was found to be 50 ohms. Calculate the equivalent conductivity of the solution. *Calcutta University B. Sc. 1979.*

$$R=\rho.\frac{l}{a} \quad \text{or,} \quad 50=\rho.\frac{1{\cdot}5}{5} \quad \therefore \quad \rho=\frac{50\times5}{1{\cdot}5}=166{\cdot}66 \text{ ohm cm.}$$

$$k=\frac{1}{166{\cdot}66}=0{\cdot}006 \text{ ohm}^{-1}\text{ cm}^{-1} \text{ or } 0{\cdot}006 \text{ mhos cm}^{-1}.$$

$$\because \quad 1 \text{ ohm}^{-1}=1 \text{ mhos.}$$

$$\lambda=k.\frac{1000}{C} \quad \text{or} \quad \lambda=\frac{0{\cdot}006\times1000}{\frac{1}{10}}=60 \text{ mhos cm}^2.$$

2. The specific conductance of an N/10 solution of NaCl at 20°C is 0·002765 mhos cm^{-1}. If the resistance of a cell containing this solution is 400 ohms, what is the cell constant ?
Cell constant = specific conductance × observed resistance = 0·002765 × 400 = 1·106.

3. Calculate the ion conductances at infinite dilution of H^+ and Cl^- ions given λ_0 (HCl) (25°C) = 426 and $t^\circ_{H^+}=0{\cdot}82$.

Burdwan University B. Sc. 1972.

According to Kohlrausch's law, λ_0 (HCl)(25°C) =

$\lambda_{H^+}+\lambda_{Cl^-}$ or $426=\lambda_{H^+}+\lambda_{Cl^-}$

Where, λ_{H^+} = ion conductance of H^+ at infinite dilution &

λ_{Cl^-} = ion conductance of Cl^- at infinite dilution.

$t^\circ_{H^+}$ = transport number of $H^+=0{\cdot}82$.

$$\text{Now, } t^\circ_{H^+}=\frac{u_{H^+}}{u_{H^+}+u_{Cl^-}}.$$

Where, u_{H^+} = ionic mobility of H^+ ;

u_{Cl^-} = ionic „ „ Cl^-.

$$= \frac{\frac{\lambda_{H^+}}{F}}{\frac{\lambda_{H^+}}{F} + \frac{\lambda_{Cl^-}}{F}} = \frac{\lambda_{H^+}}{\lambda_{H^+} + \lambda_{Cl^-}} = \frac{\lambda_{H^+}}{\lambda_\circ\,(HCl)(25^\circ C)}$$

or, $0{\cdot}82 = \frac{\lambda_{H^+}}{426}$ $\therefore$ $\lambda_{H^+} = 0{\cdot}82 \times 426 = 349{\cdot}32$ ohm^{-1} cm^2.

and $\lambda_{Cl^-} = 426 - 349{\cdot}32 = 76{\cdot}68$ ohm^{-1} cm^2.

4. An electrolyte AB dissociates as $AB = A^+ + B^-$. The equivalent conductivity at infinite dilution of AB at 25°C is 100 ohm^{-1} cm^2 eq^{-1}. Experiments on the fraction of the current carried by each ion indicate that the individual ionic conductivities of A^+ and B^- are in the ratio of 2 : 1. Find the ionic conductivities of A^+ and B^-. *Ranchi University B. Sc. 1976.*

$\lambda_\alpha(AB) = \lambda_{A^+} + \lambda_{B^-}$ ···(i) according to Kohlrausch's law.

Where, λ_α (AB) = equivalent conductance at infinite dilution ; λ_{A^+} = ionic conductance of A^+ at infinite dilution and λ_{B^-} = ionic conductance of B^- at infinite dilution.

$\frac{\lambda_{A^+}}{\lambda_{B^-}} = \frac{2}{1}$, according to the question. or, $\lambda_{A^+} = 2\lambda_{B^-}$.

Putting the value of λ_{A^+} in the equation (i),

$100 = 2\lambda_{B^-} + \lambda_{B^-}$ $\therefore$ $\lambda_{B^-} = 33{\cdot}33$ ohm^{-1} cm^2 gm ion^{-1}

and $\lambda_{A^+} = 100 - 33{\cdot}33 = 66{\cdot}67$ ohm^{-1} cm^2 gm ion^{-1}.

5. The equivalent conductances at infinite dilution ($\lambda_\circ$) of HCl, NaCl and sodium acetate are 426·2, 126·5 and 91·0 ohms^{-1} cm^2 respectively at 25°C. Calculate $\lambda_\circ$ for acetic acid.

Calcutta University B. Sc. 1972.

$\lambda_0\,(HCl) = \lambda_{H^+} + \lambda_{Cl^-}$, according to Kohlrausch's law.

$$426{\cdot}2 = \lambda_{H^+} + \lambda_{Cl^-} \quad \cdots \quad \cdots \quad (i)$$

Similarly, $126{\cdot}5 = \lambda_{Na^+} + \lambda_{Cl^-}$ ... ... (ii)

" $91{\cdot}0 = \lambda_{Na^+} + \lambda_{CH_3COO^-}$ ... (iii)

Where, λ_{H^+}, λ_{Cl^-}, λ_{Na^+} and $\lambda_{CH_3COO^-}$ are ionic conductances of H^+, Cl^-, Na^+ and CH_3COO^- at infinite dilution. On adding equation (i) and (ii) and substracting equation (ii),

$426{\cdot}2 + 91{\cdot}0 - 126{\cdot}5 = \lambda_{H^+} + \lambda_{Cl^-} + \lambda_{Na^+} + \lambda_{CH_3COO^-} - \lambda_{Na^+} - \lambda_{Cl^-}$ ∴ $390{\cdot}7 = \lambda_{H^+} + \lambda_{CH_3COO^-}$

∵ $\lambda_0 (CH_3COOH) = \lambda_{H^+} + \lambda_{CH_3COO^-}$, according to Kohlrausch's law. ∴ $\lambda_0 (CH_3COOH) = 390{\cdot}7$ ohms^{-1} cm^2 eq^{-1}.

6. A conductance cell filled with 0·01M KCl has a resistance of 2573 ohms at 25°C. The same cell filled with 0·2N acetic acid has a resistance of 5086 ohms. Calculate the dissociation constant of acetic acid.

[Specific conductance of 0·01M KCl at 25°C $= 1{\cdot}41 \times 10^{-3}$ ohm^{-1} cm^{-1}, equivalent conductance at infinite dilution of acetic acid $= 390{\cdot}7$ ohms^{-1} cm^2 eq^{-1}.] *Calcutta U. B. Sc. 1972.*

$$R = \rho.\frac{l}{a} = \frac{1}{k}\cdot\frac{l}{a} \quad \text{or} \quad 2573 = \frac{1}{1{\cdot}41 \times 10^{-3}}\cdot\frac{l}{a} \quad \therefore \frac{l}{a} = 3{\cdot}627 \text{ cm}^{-1}.$$

Now, $5086 = \rho.\ 3{\cdot}627$ ∴ $\rho = \frac{5086}{3{\cdot}627} = 1402{\cdot}26$ ohm. cm

$$\therefore\ k = \frac{1}{\rho} = \frac{1}{1402{\cdot}26} = 0{\cdot}000713 \text{ ohm}^{-1}\text{ cm}^{-1}$$ = specific conductance of 0·2N acetic acid.

$$\lambda_v = k.\frac{1000}{C} = \frac{0{\cdot}000713 \times 1000}{0{\cdot}2} = \frac{0{\cdot}713}{0{\cdot}2} = 3{\cdot}565 \text{ ohms}^{-1}\text{ cm}^2\text{ eq}^{-1}.$$

$$\alpha = \frac{\lambda_v (CH_3COOH)}{\lambda_\alpha (CH_3COOH)} = \frac{3{\cdot}565}{390{\cdot}7} = 0{\cdot}00912.$$

∴ percentage of dissociation = 0·912.

Now, $K=\frac{\frac{\alpha}{V}\cdot\frac{\alpha}{V}}{\frac{1-\alpha}{V}}$ for $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$.

$$=\frac{\alpha^2}{1-\alpha}\cdot\frac{1}{V}=\frac{\alpha^2}{1-\alpha}.C \quad \text{or,} \quad K=\frac{(0{\cdot}00912)^2\times0{\cdot}2}{1-0{\cdot}00912}$$
$$=16{\cdot}81\times10^{-6}.$$

Where, K = dissociation constant of acetic acid ; V = volume of the solution and $\frac{1}{V}=C$ = concentration of acetic acid in gm equivalent/litre.

7. A conductivity cell has electrodes 0·6 cm apart and each is of area 0·8 sq. cm. If the equivalent conductance of a saturated solution of AgCl be 130 mhos cm^2 and its solubility product $1{\cdot}06\times10^{-10}$ at any given temperature, what resistance will be registered by the saturated AgCl solution, when measured in the given conductivity cell ? *Calcutta U. B. Sc. 1974.*

$K_s=S^2$. Where, K_s = solubility product of AgCl,

S = solubility of AgCl in gm moles/litre ≡ solubility of AgCl in gm. eq/litre. $\therefore \quad S=\sqrt{K_s}=\sqrt{1{\cdot}06\times10^{-10}}=1{\cdot}029\times10^{-5}$.

$$\lambda=k.\frac{1000}{s} \quad \text{or,} \quad k=\frac{\lambda.s}{1000}=\frac{130\times1{\cdot}029\times10^{-5}}{1000}=133{\cdot}77\times10^{-9}$$

mhos cm^{-1}. Where λ = equivalent conductance at infinite dilution (saturated solution behaving as infinitely diluted solution).

$$R=\frac{1}{k}\cdot\frac{l}{a}=\frac{1}{133{\cdot}77\times10^{-9}}\times\frac{0{\cdot}6}{0{\cdot}8}=0{\cdot}0056\times10^9 \text{ ohms.}$$

8. At 25°C the specific conductivity of a saturated aqueous solution of $SrSO_4$ is $1{\cdot}482\times10^{-4}$ ohm^{-1}. cm^{-1}, while that of the water used is $1{\cdot}5\times10^{-6}$ ohm^{-1} cm^{-1}. Calculate the solubility (in equivalents/litre) of $SrSO_4$ in water at 25°C. ($\lambda_{\frac{1}{2}Sr^{++}}=59{\cdot}46$, $\lambda_{\frac{1}{2}SO_4^{--}}=79{\cdot}8$ ohm^{-1}. cm^2.) *Calcutta University B. Sc. 1972.*

$k_{SrSO_4^{=}\,soln.}=1{\cdot}482\times10^{-4}$ ohm^{-1}. cm^{-1} ;

$k_{H_2O}=1{\cdot}5\times10^{-6}$ ohm^{-1}. cm^{-1}.

$\therefore \quad k_{SrSO_4} = k_{SrSO_4 \text{ soln}} - k_{H_2O} = 1{\cdot}482 \times 10^{-4} - 1{\cdot}5 \times 10^{-6}$
$= 1{\cdot}467 \times 10^{-4}$ ohm^{-1}.cm^{-1}.

$\lambda^0_{SrSO_4} = \lambda_{\frac{1}{2}Sr^{++}} + \lambda_{\frac{1}{2}SO_4^{--}}$ from Kohlrausch's law.

$\because$ saturated solution of $SrSO_4$ is assumed to behave as infinitely diluted solution.

$$\therefore \quad \lambda^0_{SrSO_4} = \lambda_{\frac{1}{2}Sr^{++}} + \lambda_{\frac{1}{2}SO_4^{--}} = k_{SrSO_4}. \quad \frac{1000}{S}.$$

$$\text{or,} \quad 59{\cdot}46 + 79{\cdot}8 = \frac{1{\cdot}467 \times 10^{-4} \times 1000}{S} \quad \therefore \quad S = \frac{0{\cdot}1467}{139{\cdot}26}$$

$= 0{\cdot}00105$ gm eq/litre.

9. A solution of KNO_3 was electrolysed between platinum electrodes. The following results were obtained :

(i) fall in concentration of K^+ in the anode compartment $= 6{\cdot}45$ mgm/cc ; (ii) fall in concentration of NO_3^- in the cathode compartment $= 4{\cdot}87$ mgm/cc. Calculate the transport numbers of K^+ and NO_3^- ions.

$$t_{K^+} = \frac{u}{u+v}$$

$$= \frac{\text{fall in concentration around anode}}{\text{fall in concentration around anode} + \text{fall in concn around cathode}}$$

$$= \frac{6{\cdot}45}{6{\cdot}45 + 4{\cdot}87} = \frac{6{\cdot}45}{11{\cdot}32} = 0{\cdot}57. \quad \therefore \quad t_{NO_3^-} = 1 - 0{\cdot}57 = 0{\cdot}43.$$

10. A solution of silver nitrate is electrolysed between two silver electrodes. The mobility ratio of the silver and nitrate ions is 0·920. Find the transport number of Ag^+ and NO_3^- ions.

[mobility is the speed of the ion when unit potential gradient $\left(\frac{dv}{dt}\right)$ is applied. $\frac{dv}{dt}$ represents change in potential w.r.t distance between electrodes.]

$$t_- = \frac{v}{u+v} \; ; \; \frac{u}{v} = 0{\cdot}92 \text{ (according to the question)}$$

or, $\frac{u}{v}+1=0{\cdot}92+1$ or, $\frac{u+v}{v}=1{\cdot}92$ or, $\frac{v}{u+v}=\frac{1}{1{\cdot}92}$

or, $t_-=0{\cdot}52$ $\therefore$ $t_+=1-0{\cdot}52=0{\cdot}48$.

Where, u = mobility of Ag^+ ion ; v = mobility of NO_3^- ion ; t_+ = transport number of Ag^+ ion and t_- = transport number of NO_3^- ion.

11. A solution of sodium hydroxide was electrolysed between platinum elctrodes having initial concentration 0·059 gm NaOH/100 cc. After electrolysis, 100 cc of the cathode solution contained 0·06315 gm NaOH and the same current deposited 0·05216 gm silver in the coulometer. Find the transport numbers of Na^+ and OH^- ions.

Fraction of current carried by anions = fall in concn in gm equivalent/100 cc in the cathode compartment

$$=\frac{0{\cdot}059}{40}+\frac{0{\cdot}05216}{108}-\frac{0{\cdot}06315}{40}$$

$$=0{\cdot}00147+0{\cdot}000482-0{\cdot}00157=0{\cdot}000382.$$

$\because$ eq. wt of NaOH = 40 ; eq wt of Ag = 108 ;

gm eq of NaOH ≡ gm eq of Ag.

Total current carried by cations as well as anions = 0·000482

$$\therefore\quad t_-=\frac{0{\cdot}000382}{0{\cdot}000482}=0{\cdot}792.$$

$$t_+=1-0{\cdot}792=0{\cdot}208.$$

12. In a moving boundary experiment the boundary swept a volume of 0·12 cc 1(N)KCl in 1670 seconds when a current of 0·014 ampere was passed. What is the transport number of K^+ ions ?

$$Q=\frac{0{\cdot}014\times1670}{96500}=0{\cdot}000242 \text{ faradays ;}$$

$$t_{K^+}=\frac{0{\cdot}12\times1}{1000\times0{\cdot}000242}\quad\therefore\quad t_{K^+}=0{\cdot}495.$$

Problems for Practice

1. The resistance of $\frac{N}{10}$ solution of KCl occupying a volume between two platinum electrodes 1·8 cm apart and 5·4 cm^2 in area was found to be 32 ohms. Calculate the equivalent conductance of the solution. Ans. 104·1 mhos. cm.^{2}.

2. The specific conductivity of a $\frac{N}{50}$ solution of KCl at 25°C is 0·002765 mhos. If the resistance of the same solution placed in a cell is 2,000 ohms, what is the cell constant?

Kerala B.Sc. 1971. Ans. 5·53.

3. The equivalent conductivity of a 0·001028 (N) acetic acid solution is found to be 48·15 mhos at 25°C. The equivalent conductivity at infinite dilution is 390·6 mhos. Calculate the degree of dissociation of acetic acid at this concentration, and calculate the ionisation constant of the acid. *Udaipur B.Sc. 1970.*

Ans. 12·32% ; $1·78 \times 10^{-5}$.

4. A cell, whose resistance when filled with 0·1M KCl solution is 192·3 ohms, was found to be 6306 ohms when filled with $3·186 \times 10^{-3}$M NaCl solution at 25°C. Calculate (i) the cell constant (ii) the specific and equivalent conductivities of NaCl soln and (iii) the degree of dissociation of NaCl soln at this dilution.

[Given : Specific conductivity of 0·1M KCl is 0·01289 ohm^{-1}. cm^{-1} at 25°C. Equivalent conductivities of Na$^+$ and Cl$^-$ ions at 25°C are respectively 50·11 and 76·34 ohm^{-1}cm^2.]

Bombay U. B.Sc. 1970. Ans. (i) 2·479 (ii) $3·931 \times 10^{-4}$ ohm^{-1}. cm^{-1}.

5. The specific conductivity of a saturated solution of AgCN is $1·79 \times 10^{-6}$ and that of water is $0·044 \times 10^{-6}$ ohm^{-1} at 20°C. The equivalent conductivity at infinite dilution is 115·5. Calculate the solubility of AgCN in gms/litre. Ans. $2·026 \times 10^{-3}$.

6. The equivalent conductance of an aqueous solution of acetic acid is 48·15 mhos cm^2 at 25°C. If the ionic conductance of H$^+$ and CH_3OOO^- are 349·8 and 40·9 mhos respectively at

this temperature, calculate degree of dissociation of acetic acid in that solution. *Calcutta* U. *1970 B.Sc.* Ans. 12·32%.

7. Equivalent conductivity of (N) KCl solution at 18°C is 98·2 and at infinite dilution it is 131 at the same temperature. Calculate the extent of ionisation of KCl at the said dilution. *Ranchi* U. *B. Sc. 1977*. Ans. 74·96%.

8. The equivalent conductance of sodium chloride at infinite dilution is 126·45 and the transport number of cation is 0·394 at 25°C. Calculate the ion conductance of chloride ion.

Burdwan U. *B. Sc. 1968*. Ans. 76·61 $\mathrm{ohm}^{-1}\mathrm{cm}^{2}$.

9. The speed ratio of the silver and nitrate ions in a solution of $AgNO_3$ electrolysed between silver electrodes is 0·92. Find the transport number of the two ions. *Burdwan* U. *B.Sc. 1976*.

Ans. $^{t}Ag^{+} = 0{\cdot}4792$; $^{t}NO_3^{-} = 0{\cdot}5208$.

10. A 0·02M KCl solution, having a specific conductance of $27{\cdot}7 \times 10^{-4}$ mhos cm^{-1}, gives a resistance 175 ohms when measured in a certain conductivity cell. A 0·01M solution of sodium acetate in the same conductivity cell shows a resistance 575 ohms. Calculate the equivalent conductance of this sodium acetate solution. *Calcutta* U. *1975 B. Sc.*

Ans. 84·31 $\mathrm{ohm}^{-1}\mathrm{cm}^{2}\ \mathrm{eq.}^{-1}$

11. A silver nitrate solution was electrolysed in a transport cell between silver electrodes. The anode compartment contained 0·1210 gm. silver ion before electrolysis and 0·1652 gm. afterwords. During the electrolysis, 0·0854 gm. silver was deposited at the cathode. Calculate the transport numbers of Ag^{+} and NO_3^{-}. *Calcutta* U. *B. Sc. 1973.*

Ans. $^{t}Ag^{+} = 0{\cdot}4823$; $^{t}NO_3^{-} = 0{\cdot}5177$.

12. A solution of silver nitrate was electrolysed with silver electrodes. Before electrolysis 25 gms of the solution was found to contain 0·02550 gm of silver while after electrolysis 25 gms of the anode solution contained 0·04294 gm. of silver. During the process of electrolysis 0·03210 gm of silver was deposited in a silver voltameter. Calculate the transport numbers of Ag^{+} ion and NO_3^{-}.

Bombay B.*Sc. 1969*. Ans. $^{t}Ag^{+} = 0{\cdot}4878$; $^{t}NO_3^{-} = 0{\cdot}5122$.

13. In a moving boundary experiment with a 0·02(N) NaCl solution a current of 0·0016 ampere moved the boundary through a distance 6 cms in 2070 secs. The cross section of the tube is 0·1115 sq. cm. Calculate the transport number of Na^+.

Ans. $t_{Na^+} = 0{\cdot}39$.

14. At 18°C, specific conductance of a saturated solution of AgCl is $1{\cdot}12 \times 10^{-}$ $ohm^{-1}\ cm^{-1}$ (exclusive of that of water). Ionic conductances of Ag^+ and Cl^- are 54·3 and 65·5 respectively. Calculate the solubility of AgCl in gm. equivalent per litre.

Calcutta U. *B. Sc. 1950*. Ans. $0{\cdot}933 \times 10^{-5}$.

CHAPTER 0

Problems on PH of "weak electrolyte and buffer solution" and salt hydrolysis

Theory :

when the acid is weak, say HA ionising as,

$$\underset{1-\alpha}{HA} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{A^-} \quad \alpha = \text{degree of ionisation} ; C = \text{concentration} = \frac{1}{V}.$$

Where, V = volume of solution in litre.

$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2 C}{1-\alpha}$. Where, K_a = dissociation or ionisation constant of the weak acid. If the acid is very weak α can be neglected as compared to unity.

Then, $\alpha^2 C = K_a$ or $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a V}$.

But $C_{H^+} = \frac{\alpha}{v} = \alpha C = \sqrt{K_a C} = \sqrt{\frac{K_a}{V}}$.

Hence, $PH = -\log C_{H^+}$.

Similarly for a weak base like NH_4OH, $[OH^-] = \frac{\alpha}{V} = \alpha C$

$= \sqrt{K_b C} = \sqrt{\frac{K_b}{V}}$. Where, K_b = dissociation or ionisation constant of weak base. Hence, $POH = -\log [OH^-]$.

Now, $PH + POH = 14$ $\therefore$ $PH = 14 + \log [OH^-]$,

$\because$ K_w = ionic product of water $= [H^+][OH^-] = 10^{-14}$.

For a buffer solution PH can be calculated from

Henderson equation, $PH = PK_a + \log \frac{[Salt]}{[Acid]}$.

$\because$ $PKa = -\log Ka$.

For hydrolysis of salt of weak acid and strong base

e.g. sodium acetate, we have

$$NaCOOCH_3 + H_2O \rightleftharpoons CH_3COOH + NaOH$$

or $Na^+ + COOCH_3^- + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

or $\underset{(1-h)}{COOCH_3^-} + H_2O \rightleftharpoons \underset{h}{CH_3COOH} + \underset{h}{OH^-}$

h stands for degree of hydrolysis.

$K_h = \frac{K_w}{K_a} = \frac{h^2c}{1-h} \approx h^2c$. Where K_h = hydrolysis constant,

C = concentration. But $C_{OH^-} = \frac{h}{V} = hC$ $\because$ $C = \frac{1}{V}$.

Now, $C_{H^+} C_{OH^-} = K_w$

$$\text{or} \quad C_{H^+} = \frac{K_w}{C_{OH^-}} = \frac{K_w}{hc} = \frac{K_w}{\sqrt{\frac{K_w}{K_aC}}C} = \sqrt{\frac{K_aK_w}{C}}.$$

Taking logarithm of both sides,

we get, $\log C_{H_+} = \frac{1}{2} \log K_a + \frac{1}{2} \log K_w - \frac{1}{2} \log C$

or $-\log C_{H^+} = -\frac{1}{2} \log K_a - \frac{1}{2} \log K_w + \frac{1}{2} \log C$

or $PH = \frac{1}{2} PK_a + \frac{1}{2} PK_w + \frac{1}{2} \log C$

For hydrolysis of salts of strong acid and weak base

e.g. ammonium chloride,

we have, $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$

or $NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$

or $\underset{1-h}{NH_4^+} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+}$

$K = \frac{K_w}{K_b} = \frac{h^2c}{1-h} \cong h^2c$ $\because$ h is very small as compared to unity, it can be neglected.

K_b = dissociation constant or ionisation constant of weak base (NH_4OH).

$$\text{But } C_{H^+}=\frac{h}{V}=hc=\sqrt{\frac{K_w}{K_bC}}\ C=\sqrt{\frac{K_wC}{K_b}}.$$

Taking logarithm of both sides we get,

$$\log C_{H^+}=\tfrac{1}{2}\log K_w+\tfrac{1}{2}\log C-\tfrac{1}{2}\log K_b$$

$$\text{or}\quad -\log C_{H^+}=\tfrac{1}{2}\log K_b-\tfrac{1}{2}\log K_w-\tfrac{1}{2}\log C$$

$$\text{or}\quad PH=-\tfrac{1}{2}PK_b+\tfrac{1}{2}PK_w-\tfrac{1}{2}\log C$$

$$\text{or}\quad PH=\tfrac{1}{2}PK_w-\tfrac{1}{2}PK_b-\tfrac{1}{2}\log C.$$

For hydrolysis of weak acid and weak base e.g. ammonium acetate, we have $NH_4COOCH_3+H_2O\rightleftharpoons NH_4OH+CH_3COOH$

$$\text{or}\quad \underset{1-h}{NH_4^+}+\underset{1-h}{COOCH_3^-}+H_2O\rightleftharpoons \underset{h}{NH_4OH}+\underset{h}{CH_3COOH}.$$

$$K_h=\frac{K_w}{K_aK_b}=\frac{h^2}{(1-h)^2}\simeq h^2\quad\text{or}\quad h=\sqrt{\frac{K_w}{K_aK_b}}.$$

Now, $CH_3COOH\rightleftharpoons H^++CH_3COO^-$, $K_a=\dfrac{[H\ ][CH_3COO^-]}{[CH_3COOH]}$

$$\text{or}\quad K_a=\frac{[H^+](1-h)}{h}\quad\text{or}\quad K_a\approx\frac{[H_+]}{h}\quad\because\ h\text{ is neglected.}$$

$$\text{or}\quad [H^+]=h\,K_a=K_a\sqrt{\frac{K_w}{K_aK_b}}=\sqrt{\frac{K_aK_w}{K_b}}$$

Taking logarithm of both sides, we get,

$$\log C_{H^+}=\tfrac{1}{2}\log K_a+\tfrac{1}{2}\log K_w-\tfrac{1}{2}\log K_b$$

$$\text{or}\quad -\log C_{H^+}=-\tfrac{1}{2}\log K_a-\tfrac{1}{2}\log K_w+\tfrac{1}{2}\log K_b$$

$$\text{or}\quad PH=\tfrac{1}{2}PK_a+\tfrac{1}{2}PK_w-\tfrac{1}{2}PK_b$$

$$\text{or}\quad PH=\tfrac{1}{2}PK_a-\tfrac{1}{2}PK_b+\tfrac{1}{2}PK_w.$$

Solved Problems :

1. Calculate the PH of 0·1 (N) solution of an acid of dissociation constant $1{\cdot}8\times10^{-5}$.
Calcutta U. *B. Sc. 1972.*

$$\alpha=\sqrt{\frac{K_a}{c}}=\sqrt{\frac{1{\cdot}8\times10^{-5}}{0{\cdot}1}}=1{\cdot}341\times10^{-2}.$$

$[H^+] = \alpha C = 1{\cdot}341 \times 10^{-2} \times 0{\cdot}1 = 1{\cdot}341 \times 10^{-3}$.

$PH = -\log [H^+] = -\log 1{\cdot}341 \times 10^{-3} = 2{\cdot}8726$.

2. Calculate the PH of the 0·1 (N) NH_4OH solution. Given K_b for ammonia $= 1{\cdot}8 \times 10^{-5}$. *Calcutta* U. *B. Sc. 1971.*

$[OH^-] = \sqrt{K_b C} = \sqrt{1{\cdot}8 \times 10^{-5} \times 0{\cdot}1} = 1{\cdot}341 \times 10^{-3}$.

$POH = -\log [OH^-] = -\log 1{\cdot}341 \times 10^{-3} = 2{\cdot}8726$.

Now, $PH + POH = 14$ or $PH + 2{\cdot}8726 = 14$

or $PH = 14 - 2{\cdot}8726 = 11{\cdot}1274$.

3. Calculate the PH at 25°C of benzoic acid (dissociation constant at $25^\circ C = 6{\cdot}3 \times 10^{-5}$) in a 0·05 molar of benzoic acid containing 0·01 molar sodium benzoate.

$$\underset{1-\alpha}{C_6H_5COOH} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{C_6H_5COO^-}\ ;$$

$$\underset{X}{NaCOOC_6H_5} \longrightarrow \underset{X}{Na^+} + \underset{X}{C_6H_5COO^-}$$

So, we can write, $Ka = \dfrac{\alpha(\alpha + X)C}{1-\alpha} \approx \alpha(\alpha + X)C$.

Where, X is the concentration of $C_6H_5COO^-$ (benzoate anion) ions per litre from sodium benzoate ($NaCOOC_6H_5$).

Now, $6{\cdot}3 \times 10^{-5} = \alpha(\alpha + 0{\cdot}01) \times 0{\cdot}05 \quad \therefore \quad \alpha = 0{\cdot}0308$.

$[H^+] = \alpha C = 0{\cdot}0308 \times 0{\cdot}05 \quad \therefore \quad PH = -\log [H^+]$

$= -\log 0{\cdot}0308 \times 0{\cdot}05 = 2{\cdot}8125$.

4. 10 cc of 0·2 (N) NaOH is added to 30 cc of 0·1 (N) acetic acid. Calculate the PH of the resulting solution. The dissociation constant of acetic acid is $1{\cdot}8 \times 10^{-5}$. *Calcutta U. B. Sc. 1970.*

10 cc 0·2 (N) NaOH $= 10 \times 0{\cdot}2$ cc (N) NaOH $= 2$ cc (N) NaOH.

30 cc 0·1 (N) $CH_3COOH \equiv 30 \times 0{\cdot}1$ cc (N)CH_3COOH

$= 3$ cc (N)CH_3COOH.

Now, $PH = PKa + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

or, $PH = -\log 1{\cdot}8 \times 10^{-5} + \log \frac{2}{1}$ or, $PH = 5{\cdot}0457$.

5. Calculate the hydrogen ion concentration and the degree of hydrolysis in a 0·1 (M) solution of sodium acetate at 25°C $[Ka = 1{\cdot}8 \times 10^{-5}]$. *Calcutta U. B. Sc. 1978.*

$$h=\sqrt{\frac{K_w}{K_aC}}=\sqrt{\frac{10^{-14}}{1{\cdot}8\times1\;^{-5}\times0\,1}}=7{\cdot}45\times10^{-5}.$$

$$[H^+]=\sqrt{\frac{K_aK_w}{C}}=\sqrt{\frac{1{\cdot}8\times10^{-5}\times10^{-14}}{0{\cdot}1}}=1{\cdot}34\times10^{-9}\text{ gmion/litre.}$$

6. Calculate the PH of a solution of ammonium acetate ($K_{CH_3COOH}=1{\cdot}75\times10^{-5}$; $K_{NH_4OH}=1{\cdot}81\times10^{-5}$)

Calcutta U. B. Sc. 1976.

$$PH=\tfrac{1}{2}PK_a-\tfrac{1}{2}PK_b+\tfrac{1}{2}PK_w=\tfrac{1}{2}(-\log\ 1{\cdot}75\times10^{-5})-\tfrac{1}{2}(-\log\ 1{\cdot}81\times10^{-5})+(-\log 10^{-14})=7{\cdot}01.$$

Problems for practice :

1. Calculate the PH of a 0·03 (N) solution of acetic acid (dissociation constant $=1{\cdot}75\times10^{-5}$). *Calcutta U. B. Sc. 1975.*

Ans. 3·141.

2. Calculate the PH of 0·01 (N) solution of benzoic acid (dissociation constant $=6{\cdot}3\times10^{-5}$). *Calcutta U. 1977.*

Ans. 3·1004.

3. Calculate the PH of a 0·094 (N) solution of NH_4OH (dissociation constant $=1{\cdot}7\times10^{-5}$) *Calcutta* U. *B. Sc. 1977.*

Ans. 11·08.

4. Calculate the PH of a 0·05 (N) solution of NH_4OH (dissociation constant $=6{\cdot}3\times10^{-5}$) *Calcutta* U. *B. Sc. 1975.*

Ans. 10·9647.

5. The dissociation constant of acetic acid in water is $1{\cdot}8\times10^{-5}$. Calculate the hydrogen ion concentration of a solution (aqueous) which contains sodium acetate and acetic acid, the concentration of each being 0·1 (N). *Calcutta* U. *B. Sc. 1966.*

Ans. $1{\cdot}8\times10^{-5}$.

6. Calculate the degree of hydrolysis of ammonium hydroxide, dissociation constant for NH_3 is $1{\cdot}8\times10^{-5}$ and that for acetic acid is $1{\cdot}8\times10^{-5}$, ionic product of water being 1×10^{-14}. *Lucknow* U. 1963. Ans. 0·0055.

7. Calculate the percentage hydrolysis of sodium acetate in 0·1 (N) solution at 25°C. [Kacetic acid $=1{\cdot}1\times10^{-5}$ and Kw $=1{\cdot}21\times10^{-14}$]. *Calcutta* U. *B. Sc*, 1975. Ans. $1{\cdot}048\times10^{-2}$.

8. Calculate the PH of the 0·1 (N) NH_4Cl solution. Given K_b for ammonia $= 1{\cdot}8 \times 10^{-5}$. *Calcutta* U. *B. Sc. 1971.*

Ans. 5·12765.

9. A buffer is to be prepared from an acid of PKa = 4·76 at 25°C and its sodium salt. What will be the ratio of the salt to the acid in a buffer of PH = 5 at this temperature ?

Calcutta U. *B. Sc. 1979.*

[Hints. $PH = PKa + \log\frac{[\text{Salt}]}{[\text{Acid}]}$; $5 = 4{\cdot}76 + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$\therefore \frac{[\text{Salt}]}{[\text{Acid}]} = 1{\cdot}738$]

10. The percentage hydrolysis of 0·01 molar solution of sodium acetate at 25°C is 0·024. Calculate the hydrolysis constant of the salt and the dissociation constant of the acid (Ionic product of water $= 10^{-14}$). *Calcutta U. B. Sc. 1980.*

Ans. $K = 5{\cdot}8 \times 10^{-10}$; $Ka = 1{\cdot}73 \times 10^{-5}$.

CHAPTER 21

Problems on Radioactivity

Following three types of rays (or particles) are emitted from a radio-active substance : (1) α-rays or α particles : These are positively charged particles. Each α particle has the mass = 4 units and the charge carried is equal to 2. Actually they are helium nucleus ($_2He^4$). (2). β-rays or particles : These are negatively charged particles. Each β particle has the negligible mass and carries one negative charge. They are identical with electrons. (3) γ—rays : These are electromagnetic waves of very short wave length emitted from the nucleus because of transition of nucleons.

For radioactive disintegration, rate of disintegration = disintegration constant × number of atoms.

or, $N = N_0 e^{-\lambda T}$. Where, λ = disintegration constant ;

T = time ; No = initial number of atoms and

N = number of atoms present time to time from the very commencement of the disintegration.

or, $\lambda = \frac{2 \cdot 303}{T} \log \frac{No}{N}$.

Time for half change (half life period), $T_{\frac{1}{2}} = \frac{0 \cdot 693}{\lambda}$.

Average life period $= \frac{1}{\text{disintegration constant}} = \frac{1}{\lambda}$.

In radio-active equilibrium : $\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1}$.

1 curie = $3 \cdot 7 \times 10^{10}$ disintegrations/sec.

Solved Problems :

1. Uranium—238 (atomic number 92) during various disintegration steps loses 8α and 6β particles. What will be the atomic weight and atomic number of the new products ?

Punjab U. *1967.*

We know that when 1α particle is emitted, atomic weight of the element decreases by 4 units and atomic number by 2 units. On the other hand when 1 β particle is emitted, atomic weight of the element remains unchanged but atomic number increases by one. As $_{92}U^{238}$ loses 8α particles, its atomic weight decreases by $8 \times 4 = 32$ units and atomic number by $8 \times 2 = 16$ units. So, the atomic weight of the new element $= 238 - 32 = 206$ and the atomic number $= 92 - 16 = 76$. Again, this new element further loses 6β particles, the atomic weight of the element, obtained by the emission of β particles $= 206$ but the atomic number of the element $= 76 + 6 = 82$.

2. Calculate the number of alpha particles emitted/sec by one gm of pure thorium oxide. (Half—life of thorium—232 is $1 \cdot 39 \times 10^{10}$ years and Avogadro's No $6 \cdot 02 \times 10^{23}$). *Poona* U. *1968.*

$$T_{\frac{1}{2}} = \frac{0 \cdot 693}{\lambda} \quad \text{or} \quad \lambda = \frac{0 \cdot 693}{1 \cdot 39 \times 10^{10} \times 365 \times 24 \times 60 \times 60}$$

$$= 1 \cdot 5 \times 10^{-18} \text{ sec}^{-1}.$$

264 gms (1 gm mole ThO_2) of thorium oxide contain $6{\cdot}02\times 10^{23}$ atoms of Th.

∴ 1 gm „ „ contains $\frac{6{\cdot}02\times 10^{23}}{264}$ „ „

Now, rate of disintegration $=\lambda\times$ number of atoms,

or, rate of disintegration $=\frac{1{\cdot}5\times 10^{-18}\times 6{\cdot}02\times 10^{23}}{264}$

$=3{\cdot}42\times 10^{3}\ \text{sec}^{-1}$

∴ the number of alpha particles emitted/sec by one gm of pure thorium oxide $=3{\cdot}42\times 10^{3}$.

3. A piece of wood recovered in an excavation, has 25·6% as much $_6C^{14}$ as ordinary wood today has. When did this piece get buried ? $T_{\frac{1}{2}}$ for $_6C^{14}=5760$ years. *I. I. T. 1969.*

Here, $N_0=100$; $N=25{\cdot}6$.

$$\lambda=\frac{0{\cdot}693}{T_{\frac{1}{2}}}=\frac{0{\cdot}693}{5760}=1{\cdot}203\times 10^{-4}\ \text{years}^{-1}.$$

$$\text{Now,}\ \lambda=\frac{2{\cdot}303}{T}\log\frac{N_0}{N}\quad\text{or}\quad T=\frac{2{\cdot}303}{1{\cdot}203\times 10^{-4}}\log\frac{100}{25{\cdot}6}$$

$=11{,}330$ yrs.

4. The half life of a radio element is 231 minutes. How long will it take for $\frac{9}{10}$ th fraction of the element to decay ?

Calcutta U. 1970.

$$\lambda=\frac{0{\cdot}693}{231}=3\times 10^{-3}\ \text{minute}^{-1}.\quad \frac{N}{N_0}=\frac{1}{10}.$$

$$\text{Now,}\ \lambda=\frac{2{\cdot}303}{T}\log\frac{N_0}{N}\quad\text{or}\quad 3\times 10^{-3}=\frac{2{\cdot}303}{T}\log 10=\frac{2{\cdot}303}{T}$$

$$\therefore\quad T=\frac{2{\cdot}303}{3\times 10^{-3}}=767{\cdot}6\ \text{minutes}.$$

5. At radio active equilibrium, the ratio between atoms of the two radioactive elements A and B was found to be $3{\cdot}1\times 10^{9}:1$ respectively. If the half period of element A is 2×10^{10} years, what is the half-life period of the element B.

Mysore U. *1971.*

$$\frac{N_A}{N_B}=\frac{\lambda_B}{\lambda_A}=\frac{\frac{0{\cdot}693}{T_{\frac{1}{2}}(B)}}{\frac{0{\cdot}693}{T_{\frac{1}{2}}(A)}}=\frac{T_{\frac{1}{2}}(A)}{T_{\frac{1}{2}}(B)}\text{ or, }\frac{3{\cdot}1\times10^9}{1}=\frac{2\times10^{10}}{T_{\frac{1}{2}}(B)}$$

$$\therefore\ T_{\frac{1}{2}}(B)=\frac{2\times10^{10}}{3{\cdot}1\times10^9}=6{\cdot}451\text{ years.}$$

Problems for practice :

1. Radioactive element actinium (atomic weight 227, atomic number 89) undergoes a series of disintegrations leading to the formation of lead of atomic weight 207 (atomic number 82). How many alpha and beta emissions are involved ? *Bombay U.* 1962. Ans. 5α-particles ; 3β-particles.

2. The atomic weight of thorium (Th) is 232 and atomic number=90. How many α and β particles should be emitted so that we may have an isotope of lead with atomic weight=208 and atomic number=82 ? *Bombay U.* 1968. Ans. 6 α-particles ; 4β-particles.

3. By natural radioactivity ${}_{92}U^{238}$ undergoes the following change : ${}_{92}U^{238}\rightarrow UX_1+\alpha$ particle ... (i)

$UX_1\rightarrow UX_2+\beta$ particle ... (ii)

Determine the atomic mass number of UX_1 and UX_2.

Gorakhpure U. 1970. Ans. same atomic mass number but different in atomic number.

4. 1 gm of pure ThO_2 emits 3600α-particles per second. The half life period of Th is $1{\cdot}39\times10^{10}$ years. Calculate the Avogadro's number. (O=16, Th=232). *Bombay* U. 1974. Ans. $6{\cdot}015\times10^{23}$.

5. A radio isotope decays at such a rate that after 69 minutes, only a quarter of the original substance remains. Calculate the disintegration constant and half life of the radio isotope. *Poona* U. 1968. Ans. $3{\cdot}33\times10^{-4}$; $0{\cdot}208\times10^4$ sec.

6. The half life of uranium is $4{\cdot}51\times10^9$ years. Calculate its disintegration constant. *Lucknow* U. 1968. Ans. $1{\cdot}55\times10^{-10}$ years^{-1}.

7. The half life period of a radio-element is 6·93 hrs. How long will it take to reduce its activity to one-tenth of its original value ? *Bombay* U. 1974. Ans. $3{\cdot}762\times10^{-2}$.

8. The half-life of $_6C^{14}$ is 5570 years. What fraction of the original $_6C^{14}$ would still remain after 10,000 yrs ? *Calcutta* U. *B. Sc.* 1975. Ans. 0·3.

9. Calculate the number of disintegrations/sec obtainable from 1 gm $_{90}Th^{232}$, given that the disintegration constant for $_{90}Th^{232}$ is $1{\cdot}58\times10^{-18}$ sec^{-1}. *Bombay* U. 1975. Ans. $4{\cdot}098\times10^{3}$.

10. A radio-isotope has a 5-year half life. After a given amount decays for 15 years, what fraction of the original isotope remains ? *Indian School Certificate Examination*, 1978. Ans. $\frac{1}{8}$.

11. Radium D, a radioactive isotope of lead, emits beta rays with a half life of approximately 20 years. If 20 mg of this radio isotope is stored, how much of it will be left behind after 60 years ? *Indian School Certificate Examination*, 1978. Ans. 2·5 mg.

12. Half life period of radium is 1600 yrs, findout the disintegration constant and average life period (To). U. *Pradesh I. Sc.* 1977. Ans. $4{\cdot}33\times10^{-4}$ per yr. ; 2309 yrs.

$$\left(\text{Hint. } T_o=\frac{1}{\text{disintegration constant}}\right)$$

13. Half life period of polonium is 140 days, in what time 1 gm of polonium changes to $\frac{1}{4}$ gm ? U. *P. I. Sc.* 1978. Ans. 280 days.

14. The half life period of uranium—237 is $2{\cdot}5\times10^{5}$ yrs. After how many years will the mass of uranium become 25% of its original mass. U*ttar Pradesh. I. Sc.* 1976. Ans. 5×10^{5}.

15. The half life period of an element is 10 yrs. Will the element totally disappears in the next 20 yrs ? Explain with reasons. U. *P. I. Sc.* 1978S. Ans. Total quantity of a radioactive element will disintegrate after infinite period.

16. Below are given the structures of four atomic nuclei. (i) 8P+8*n* (ii) 8P+9*n* (iii) 20P+20*n* (iv) 18P+22*n*. From

these choose those that are isotopic and those that are isobaric. *Uttar Pradesh Inter Board* 1977S.

[Hint : Isotopes have same at no but have different at wts. So, (i) and (ii) are isotopes. Isobars have different at. nos but have same at wt. so, (iii) and (iv) are isobars.]

17. Binding energy of ${}_2He^4$ is 28·57 Mev. What will be the binding energy per nucleon for this element ? U. *P. I. Sc.* 1978.

[Hint. Binding energy of ${}_2He^4$/nucleon$=\dfrac{\text{Binding energy}}{\text{number of nucleons}}$

$$=\frac{28{\cdot}57}{4}=7{\cdot}14 \text{ Mev.}\Big]$$

18. Mass number of an element is 209 and its atomic number is 83. If an atom of this element emits an alpha (α) and a beta (β) particle in succession ; then findout the mass number and atomic number of the new element formed. *Uttar Pradesh Inter Board.* 1978. [Hint. When an alpha particle is ejected from the nucleus, the new atom will have at wt less by 4 and at no less by 2. ∴ at wt (mass number) of new element$=209-4=205$ and at no of new element$=83-2=81$. On the ejection of a beta particle there is no difference in at wt but at no increases by 1.]

19. $X \xrightarrow{-\alpha} Y \xrightarrow{-2\beta} Z$. What is the relation between X and Z in the equation. U. *P. I. Sc.* 1977S. Ans. X & Z are isotopes.

20. Mass number and atomic number of an atom are 232 and 90 respectively. After emitting two β particles how many α particles it should emit so as to get an atom having mass number and atomic number 212 and 82 respectively. *Uttar Pradesh I. Sc.* 1978. Ans. 5α.

21. How many α and β particles will be ejected in all in the conversion of the nucleus ${}^{232}_{90}X$ to ${}^{208}_{82}Y$? *Kanpur* 1970. Ans. 6α & 4β.

22. The atom of an element X with At. No. 15 and mass No. 31, absorbs one neutron when irradiated with neutrons and is converted to its radioactive isotope Y which is a beta emitter.

Isotope Y then decays and changes to an element Z which forms a gaseous hydride of formula ZH_2. (i) Deduce the Mass No. and At. No. of Z.

(ii) What is the molecular wt. of ZH_2 ?

(iii) To which groups of the periodic table do X, Y and Z belong ?

(b) Radioactive Uranium (At. wt. 238, At. No. 92) undergoes a series of disintegrations leading to the formation of lead (At. wt. 206, At. No. 82). How many α and β emissions are involved in the process ? *Calcutta* U. *B. Sc*. 1980 (New).

[Hints : $^{31}_{15}X + ^{1}_{0}n \rightarrow ^{32}_{15}Y \xrightarrow{-\beta} ^{32}_{16}Z$. (i) Mass No of Z = 32 and At. No. of Z = 16. (ii) Mol. wt. of $ZH_2 = 32 + 2 \times 1 = 34$. (iii) X, Y belong to group V and Z belongs to group VI of the periodic table.

(b) Transition $^{238}_{92}U \rightarrow ^{206}_{82}Pb$. Loss in mass number = 238 − 206 = 32. Decrease in atomic number = 92 − 82 = 10. Loss in mass number can be set for α—particle emissions. Since each particle accounts for a decrease of 4 units, numder of α—particles corresponding to a decrease of 32 will be 8. When 8α—particles are lost by a nuclide, its atomic number should decrease by 16. Actual decrease observed is 10. To account for the difference of 6 in atomic numbers there should be a loss of 6 β – particles also. Therefore : number of α – particles lost = 8 ; no of β—particles lost = 6.]

23. The disintegration rate of a radio active element changes from an initial value of 3112 disintegrations per minute to 980 disintegrations per minute in 42 days. Calculate the disintegration constant and half life period for this element.

Ans. 25·1 days, 0·02752 days^{-1}.

24. Calculate the age in the following cases : (i) A piece of hair in which C – 14 activity is 60% of the activity found to-day ($t_{\frac{1}{2}}$ = 5,760 yrs). *I. S.C. E.* 1980. (ii) A vegetarian beverage whose tritium content is only 5% of lead in living plants ($t_{\frac{1}{2}}$ = 12·3 yrs).

Ans. (i) $4·256 \times 10^3$ yrs, (ii) 53·31 yrs.

25. One microgram of Na – 24 is injected into the blood of a patient. How long will it take the radio activity to fall to 10% of initial value ? ($t_{\frac{1}{2}}=14·8$ hrs for Na—24).

Ans. 2·05 days [1 microgram $=10^{-6}$ gram]

26. A radio active element A emits alpha rays and is converted to another radio active element B which is a beta emitter. B is changed to C which is another beta emitter. The final product formed is D (i) If the mass number of A is 238 and its atomic number is 92 deduce the mass numbers and atomic numbers of B, C and D. (ii) If A belongs to group VI of the Periodic Table indicate the groups to which B, C and D belong. *I. S. C. E. 1979.* Ans. (i) mass nos. 234, 234, 234 ; at. nos 236, 237, 238 (ii) IV, V, VI.

27. A radio active element ${}_{86}X^{226}$ losses one Alpha (α) particle, then emits successively two Beta (β) particles. What will be the Mass number and Atomic number of the new element ? What will the new element be called in relation to the original element ? *W. B. J. E. E. 1980.*

Ans. 222 ; 86 and isotope.

28. Complete the following nuclear reaction equations :—

(i) ${}^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + (\qquad)$ (ii) ${}^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow {}^{30}_{15}\text{P} + (\qquad)$

I. S. C. E. 1979.

Ans. (i) ${}^{4}_{2}\text{He}$; (ii) ${}^{1}_{0}n$.

29. Complete the following nuclear reaction equations

(i) ${}^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{140}_{56}\text{Ba} + (\,) + 2{}^{1}_{0}n$

(ii) ${}^{27}_{13}\text{Al} + (\,) \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}n$

I. S. C. E. 1980. Ans. (i) ${}^{94}_{36}\text{Kr}$ (ii) ${}^{4}_{2}\text{He}$.

CHAPTER 22

Problems on Organic formula, determination of mol. wt and percentage composition

Solved Problems with theory :

1. 0·2 gm of anhydrous organic acid gave on combustion 0·04 gm water and 0·195 gm carbon dioxide. The acid is found to be dibasic and 0·5 gm of its silver salt leaves on ignition 0·355 gm silver. What is the molecular formula of the acid ?

M gm silver salt contains 2×108 gm silver [Molecular wt. of silver salt=M ; as acid is dibasic, formula of the acid is RH_2. Where R stands for remaining portion of the dibasic acid. It therefore forms silver salt as RAg_2. For mol. wt of acid consider $RH_2 \rightarrow RAg_2 - 2Ag + 2H$]

0·5 gm silver salt contains 0·355 gm silver

M gm „ „ „ $\frac{0{\cdot}355}{0{\cdot}5} \times M$ „

$\therefore \frac{0{\cdot}355 \times M}{0{\cdot}5} = 2 \times 108 \quad \therefore M = \frac{2 \times 108 \times 0{\cdot}5}{0{\cdot}355} = 304{\cdot}2$

$\therefore$ mol. wt of the acid $= 304{\cdot}2 - 2 \times 108 + 2 = 90{\cdot}2$

% of carbon $= \frac{0{\cdot}195 \times 12}{44} \times \frac{100}{0{\cdot}2} = 26{\cdot}59$.

„ „ hydrogen $= \frac{0{\cdot}040 \times 12}{18} \times \frac{100}{0{\cdot}2} = 2{\cdot}22$.

„ „ oxygen $= 100 - (26{\cdot}59 + 2{\cdot}22) = 71{\cdot}19$.

Calculation of emperical formula

Name of the element in orgc. compound	%	$\frac{\%}{\text{At wt}}$	Number obtained in previous colm/ least number	Number of atoms	Emperical formula
Carbon (C)	26·59	$\frac{26{\cdot}59}{12} = 2{\cdot}22$	$\frac{2{\cdot}22}{2{\cdot}22} = 1$	1	CHO_2
Hydrogen (H)	2·22	$\frac{2{\cdot}22}{1} = 2{\cdot}22$	$\frac{2{\cdot}22}{2{\cdot}22} = 1$	1	
Oxygen (O)	71·19	$\frac{71{\cdot}19}{16} = 4{\cdot}45$	$\frac{4{\cdot}45}{2{\cdot}22} = 2$	2	

Calculation of molecular formula

Let exact formula of the compound be $(CHO_2)n$. Where, n=a positive full number. Now, wt of $(CHO_2)n$=mol. wt of the compound. $(12+1+32)n=90{\cdot}2$ ∴ n=2.

∴ molecular formula of the dibasic organic acid is $C_2H_2O_4$.

2. When heated carefully, 0·3652 gm of silver salt of an organic monobasic acid gave 0·1720 gm silver. Find the molecular weight of the organic acid.

0·1720 gm silver is obtained from 0·3652 gm silver salt

108 „ „ „ „ „ $\frac{0{\cdot}3652}{0{\cdot}172}\times 108$ „ „ .

As 1 gm equivalent silver is obtained from 1 gm equivalent of silver salt, $\frac{0{\cdot}3652\times108}{0{\cdot}172}=229{\cdot}2$ gms is the equivalent wt of the silver salt. Now, equivalent weight of the acid = equivalent weight of the silver salt—equivalent wt of Ag+equivalent wt of hydrogen.

∴ equivalent weight of the organic acid $=229{\cdot}2-108+1$
$=122{\cdot}2$

∵ equivalent weight of Ag=108; equivalent weight of hydrogen=1.

Mol. wt of the acid=eq. wt.×basicity$=122{\cdot}2\times1=122{\cdot}2$

∵ basicity of the organic acid=1.

3. When heated cautiously in a crucible, 0·759 gm of the silver salt of a dibasic organic acid, yielded 0·463 gm silver. Calculate the molecular weight of the organic acid.

0·463 gm silver is left when 0·759 gm silver salt of the acid is heated.

108 gm „ „ „ „ $\frac{0{\cdot}759\times108}{0{\cdot}463}=177{\cdot}05$ gm „ „

∴ equivalent weight of the silver salt of the acid=177·05.

∵ equivalent weight of silver=108.

The equivalent weight of the acid $=177{\cdot}05-108+1=70{\cdot}05$

∴ molecular weight of the acid $=70\ 05\times2=140{\cdot}10$.

Determination of molecular weight of bases by platinichloride method.

Theory : Many organic bases generally amines react with chloroplatinic acid (H_2PtCl_6) to form chloroplatinic salt having formula $B_2H_2PtCl_6$, where B represents symbol for one equivalent of the base. Chloroplatinic salt on heating decomposes to platinum (Pt) as residue according to the reaction $B_2H_2PtCl_6 \rightarrow Pt$.

Let the weight of the chloroplatinic acid salt be a gms.

Let the weight of platinum left after heating be b gms.

Now, M gm chloroplatinic salt contain 1 gm atom platinum,

i.e, M gm " " " 195 gm platinum

$\because$ M = molecular weight of the chloroplatinic salt ; at. wt of platinum = 195.

$\therefore$ a " " " $\frac{195 \times a}{M}$ gm platinum.

Hence, $\frac{195 \times a}{M} = b$ or $M = \frac{195 \times a}{b}$.

The equivalent weight of the base represented by B

$$= \frac{\text{molecular weight of } B_2H_2PtCl_6 - \text{molecular weight of } H_2PtCl_6}{2}$$

$$= \frac{\text{mol. wt of } B_2H_2PtCl_6 - 410}{2} = \frac{\frac{a \times 195}{b} - 410}{2}.$$

Molecular weight of the base = equivalent weight of the base × acidity of the base $= \left(\frac{\frac{a}{b} \times 195 - 410}{2}\right) n.$

Where, n represents acidity of the base.

Solved Problems :

4. Calculate the molecular weight of a monoacidic base, 0·596 gm chloroplatinic acid salt of the base on ignition leaves 0·195 gm platinum as residue.

Mol. wt of the salt $= \frac{195 \times 0{\cdot}596}{0{\cdot}195} = 596$

$\therefore$ mol. wt of the base $= \left(\frac{596 - 410}{2}\right) \times 1 = 92{\cdot}9$

$\because$ n = 1 = acidity.

5. Calculate the molecular weight of a diacidic base, 0·98 gm chloroplatinic acid salt of the base on ignition leaves 0·3585 gm platinum as residue.

$$\text{Mol. wt of the salt} = \frac{195 \times 0{\cdot}98}{0{\cdot}3585} = 533.$$

$$\text{Equivalent wt. of the base} = \frac{533 - 410}{2} = 61{\cdot}5$$

$\therefore$ mol. wt of the base $= 61{\cdot}5 \times 2 = 123$

$\therefore$ acidity $= 2$.

Problems for practice

1. An organic compound containing C, H and Cl gave the following results on analysis : (i) 2·4 gms of the compound on combustion gave 0·88 gm of CO_2 and 0·1728 gm of H_2O, (ii) 0·117 gm of the compound when heated with conc. HNO_3 and $AgNO_3$ in a Carius furnace gave 0·42 gm of AgCl. Calculate the percentage composition of the elements present in the compound. U. *P.* *1976*. Ans. %C=10 ; %H=0·8 ; %Cl=88·8.

2. A monobasic organic acid gave on combustion the following percentage composition : Carbon 39·95 and hydrogen 6·69. 0·2565 gm of the silver salt of the acid gave on ignition 0·1659 gm of silver. Calculate the molecular formula of the acid. *Andhra* U. *B. Sc.* Ans. C_3H_7COOH.

3. 0·6387 gm of the platinichloride of a monoacid base on ignition gave 0·209 gm of platinum. Find the molecular weight of the base. (Pt=195) Ans. 93.

4. 1·9 gms of the silver salt of a dibasic acid gave 1·08 gms of silver on ignition. Calculate the molecular weight of the acid. Ans. 166.

5. A chloroplatinate of a saturated aliphatic mono-amine was found to contain 19% of platinum. Calculate the molecular weight of the amine. Calcutta University B. Sc. Ans. 210·5.

6. The platinichloride salt of a mono acid organic base yielded 24·6% metallic platinum on ignition. Calculate the molecular weight of the base. Ans. 93·84.

7. A monobasic organic acid on combustion gave the following percentage composition : C=39·95, H=6·69. 0·2565 gm of the silver salt of the acid gave on ignition 0·1659 gm of silver. Calculate the molecular formula of the acid. *Roorkee* 1973. Ans. $C_2H_4O_2$.

8. An organic compound contains 66·7% of carbon, 7·4% of hydrogen, 0·135 gm of the same substance yielded 27·9 ml of N_2 at N. T. P. Determine the empirical formula of the compound. *Uttar Pradesh I. Sc.* 1977S. Ans. C_3H_4N.

9. An organic compound gave the following results on analysis : (i) 0·76 gm of compound on combustion gave 0·44 gm of CO_2 and 0·36 gm of H_2O. (ii) 0·151 gm of the compound on heating with conc. HNO_3 and $BaCl_2$ produced 0·465 gm of $BaSO_4$. Calculate the percentage composition of the elements present in the given compound. U. *P.* 1976. Ans. %C=15·79, %H=5·26 and %S=42·38.

10. 1·09 gm of an organic compound on combustion gave 0·88 gm CO_2 and 0·45 gm water. 0·218 gm of the substance on boiling with HNO_3 and adding $AgNO_3$ gave 0·376 gm AgBr. Calculate the percentage of C, H and Br in the compound. U. P. 1978S. Ans. %C=22 ; %H=4·6 ; %Br=73·4.

11. An organic compound gave the following results on analysis. (i) 0·369 gm of the compound on combustion gave 0·396 gm of CO_2 and 0·189 gm of H_2O. (ii) 0·246 gm of the same substance gave 0·379 gm AgBr. Calculate the percentage of C, H and Br in the given compound. U. *P.* 1977S.

Ans.. %C – 29·27, %H=5·69, %Br=65·55.

SI UNITS (Systeme internationale)

Physical quantity	*Name of unit*	*Symbol for unit*
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mole
Energy	joule	J
Electric charge	coulomb	C
Electric potential difference	volt	V
Electric resistance	ohm	Ω
Customary temperature	celsius	°C
Area	square meter	m^2
Volume	cubic meter	m^3
Density	kilogram per cubic meter	kgm^{-3}
Pressure [Pa (pas cal) has been suggested as the name]	newton per square metre	$Nm^{-2} = kgm^{-1}$
Heat capacity	joule per kelvin	$JK^{-1} = kgm^2.s^{-2}K^{-1}$
Mass of an atom	Atomic mass unit	amu

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	6	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	3	5	8	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	17	19	21
						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

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52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 2	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2	3 4 5	5 6 7
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59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
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61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 4 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 3 4	5 6 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 3 4	5 5 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 3 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	4 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	2 3 4	4 5 6
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72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	2 3 4	4 5 5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
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78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
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81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
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85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0 1 1	2 2 3	3 4 4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
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97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 4 4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1	2 2 3	3 3 4

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·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0 0 1	1 1 1	2 2 2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0 0 1	1 1 1	2 2 2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0 0 1	1 1 1	2 2 2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0 1 1	1 1 2	2 2 2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0 1 1	1 1 2	2 2 2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0 1 1	1 1 2	2 2 2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0 1 1	1 1 2	2 2 2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0 1 1	1 1 2	2 2 3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0 1 1	1 1 2	2 2 3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0 1 1	1 1 2	2 2 3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0 1 1	1 2 2	2 2 3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0 1 1	1 2 2	2 2 3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0 1 1	1 2 2	2 3 3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0 1 1	1 2 2	2 3 3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0 1 1	1 2 2	2 3 3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0 1 1	1 2 2	2 3 3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0 1 1	1 2 2	2 3 3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0 1 1	1 2 2	2 3 3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0 1 1	1 2 2	3 3 3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0 1 1	1 2 2	3 3 3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0 1 1	2 2 2	3 3 3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0 1 1	2 2 2	3 3 3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0 1 1	2 2 2	3 3 4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0 1 1	2 2 2	3 3 4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0 1 1	2 2 2	3 3 4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0 1 1	2 2 3	3 3 4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0 1 1	2 2 3	3 3 4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0 1 1	2 2 3	3 4 4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0 1 1	2 2 3	3 4 4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0 1 1	2 2 3	3 4 4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0 1 1	2 2 3	3 4 4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0 1 1	2 2 3	3 4 4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0 1 1	2 2 3	3 4 4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1 1 2	2 3 3	4 4 5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1 1 2	2 3 3	4 4 5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1 1 2	2 3 3	4 4 5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1 1 2	2 3 3	4 4 5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1 1 2	2 3 3	4 4 5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1 1 2	2 3 3	4 5 5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1 1 2	2 3 4	4 5 5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1 1 2	2 3 4	4 5 5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1 1 2	2 3 4	4 5 6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1 1 2	3 3 4	4 5 6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1 1 2	3 3 4	4 5 6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1 1 2	3 3 4	5 5 6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1 1 2	3 3 4	5 5 6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1 1 2	3 3 4	5 5 6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1 1 2	3 4 4	5 6 6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1 1 2	3 4 4	5 6 6

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
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·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
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·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
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·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
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·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
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·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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